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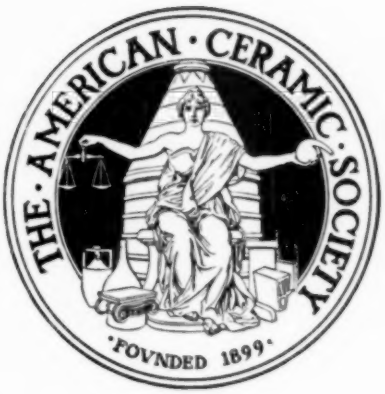

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THE AMERICAN CERAMIC SOCIETY

Vol. 28 January 1, 1945 No. 1

VARIATIONS OF REFRACTIVE INDEX OF GLASS WITH TIME AND TEMPERATURE IN ANNEALING REGION*

By Harold A. McMaster

Abstract

The refractive index of a rapidly cooled fiber of borosilicate glass was found to increase according to the equation, $1/(N_e - N) - 1/(N_e - N_0) = At$, where t is time, N_e is equilibrium index, and A is a constant at constant temperature. Index data were plotted according to this equation to determine, graphically, values of N_e and A for several temperatures between 914° and 1060°F. Values of N_e for temperatures from 1060° to 1180°F. were determined by prolonged heating of the glass at each 20° interval. The change of A with temperature was found to be well represented by the equation, $\log A = K/T + C$, where T is the absolute temperature and K and C are constants.

I. Introduction

The properties and behavior of glass in the annealing region have been studied from many viewpoints in the last twenty-five years. Many papers[1] have been written on the anomalous behavior of such properties as refractive index, density, thermal expansion, strain, and viscosity. The current demand for high-precision optical glass has caused renewed interest in the behavior of refractive index during annealing. The present paper is a detailed study of the variations of refractive index of a borosilicate glass with time and temperature in the annealing region.

Winter[1] found that glass has a high-temperature state with a low index and a low-temperature state with a high index. Glass which has been suddenly chilled from a softened condition has a low index corresponding to the high-temperature state. If the same piece of glass is reheated and then cooled very slowly, that is, well annealed, its index will approach a maximum value characteristic of the low-temperature state. The transformation from one state to the other occurs in a rather well-defined temperature region. At each temperature in this region, the glass has a characteristic equilibrium index, N_e, as shown in Fig. 1, which can be found by simultaneously heating a low-index or chilled sample of glass and a high-index or well-annealed sample until the indices of both samples reach the same value.

II. Problem

The present study concerns chiefly the manner in which the low index of a chilled or poorly annealed glass increases to equilibrium. It is important to know how the index increases during annealing when a high, stable, and uniform value of index is desired for high-precision optical glass. One purpose of the present study is to derive the basic equations for a quantitative approach to index annealing.

III. Apparatus

The measurements were made on small rods or fibers of borosilicate glass, 0.5 to 1.0 mm. in diameter, all of which were sections of a single long fiber to assure

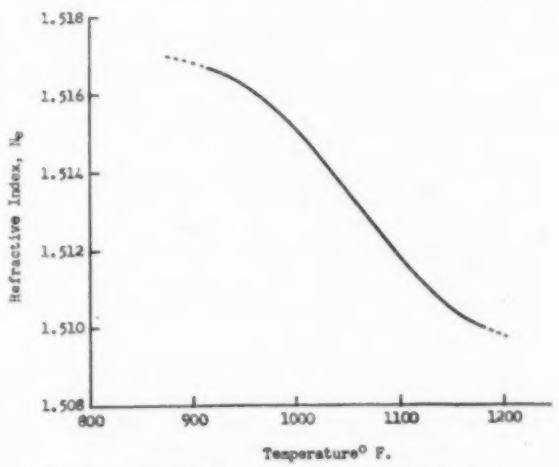

Fig. 1.—Equilibrium index in annealing region.

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Glass Division). Received June 10, 1944.

[1] For bibliography, see footnote references to paper by Aniuta Winter, "Transformation Region of Glass," *Jour. Amer. Ceram. Soc.*, **26** [6] 189–200 (1943).

practically identical composition and thermal history. The index of the fibers as drawn corresponded to the high-temperature state and was about 0.0075 lower than the fine-annealed index of the same glass.

The sodium D index of the fibers was measured by immersion in an apparatus patterned after that of Faick and Fonoroff.[2] The index of the liquid in most cases could be matched to that of the fiber more accurately than the index of the liquid could be measured by a Bausch and Lomb precision refractometer. A slight error, however, occurred in matching newly drawn fibers because they were not uniform in index until partially annealed. The refractometer scale correction was determined by reference to a standard borosilicate prism whose index had been determined to the sixth decimal place on a spectrometer at the National Bureau of Standards.

Heating was provided either by a muffle furnace or a small cylindrical furnace equipped with a commercial-type automatic control. The thermocouple in both cases was inclosed by a hollow steel block and the fibers were placed close to or in contact with the thermocouple.

IV. Procedure

The procedure was (*a*) to measure the index of a chilled fiber, (*b*) to insert the fiber into the furnace held at a selected temperature, (*c*) to heat the fiber for a measured interval of time, (*d*) to withdraw the fiber rapidly to freeze in the higher index resulting from the heating, and (*e*) to measure the index again at room temperature. This process was repeated, usually with increasing heating intervals, until the index was increasing very slowly compared with its initial rate, indicating that equilibrium had been closely approached.

For temperatures above 1060°F., the index increased so rapidly that it could not be followed accurately by the foregoing procedure, and only the maximum index, or N_e, values were obtained for each temperature. Above 1180°F., the index changed so rapidly that even the N_e values could not be obtained accurately because the index would increase during chilling of the fiber.

V. Results

The indices resulting from various heating intervals at temperatures from 914° to 1060°F. are summarized in Table I. The time required to take a set of measurements varied from 750 hours at 914°F. to 20 minutes at 1060°F. Optimum conditions were met at about 1020°F., where the complete set of data could be taken in a short enough time that calibrations of the refractometer and temperature controller would not change appreciably and yet the heating intervals were long enough that the time required for the fiber to heat was negligible.

Figure 2 is a graph of the data shown in Table I, column (6) for 1020°F. The index is increasing very slowly near 100 minutes and seems to be approaching a maximum or equilibrium value in a uniform manner. By assuming a value for N_e and plotting $1/(N_e - N)$ against time, the graph in Fig. 3 is obtained as a nearly straight line. The empirical law expressed by this graph is shown in equation (1).

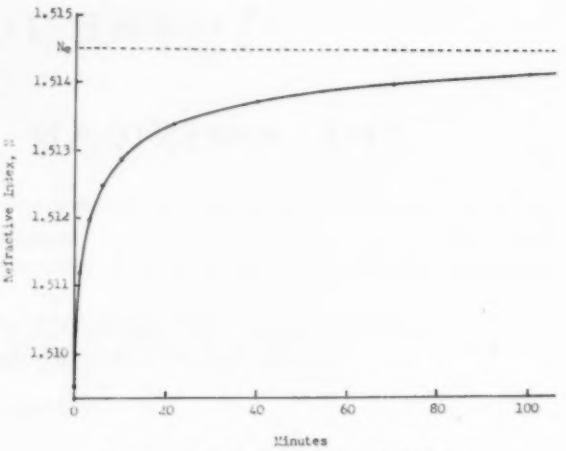

FIG. 2.—Increasing index at 1020°F.

$$\frac{1}{N_e - N} - \frac{1}{N_e - N_0} = At \qquad (1)$$

N_0 = initial index.
N = index after time, t.
A = rate or slope constant, function of temp. only.

If N_e is chosen too low, the line will curve upward and vice versa. The measured change of index was 0.0046 and the extrapolation to N_e was only 0.0004 with an accuracy of closer than ±0.0001. At 914°F., where it was more difficult to maintain a constant temperature throughout the experiment, the extrapolation of N_e was probably reliable only to ±0.0002.

Equation (1) agrees with the data within the limits of experimental error except for the initial curvature. Winter[3] has proposed an exponential equation for increasing index, but equation (1) agrees with the present data more closely than the exponential equation does. Equation (1) is of the same form as the Adams and Williamson[4] equation for the release of strain, which has been interpreted by Taylor[5] as indicating the presence of a bimolecular reaction.

Graphs such as that shown in Fig. 3 were prepared for all eight sets of data in order to obtain N_e and A for each temperature. These graphically determined values of N_e and A are given in Table II. The graphically determined values of N_e from Table II and the experimental values from Table III make up the smooth curve of Fig. 1. The difference between the graphical and experimental values of N_e is only 0.00009 at 1060°.

[2] C. A. Faick and Bernard Fonoroff, "Precision Apparatus for Rapid Determination of Indices of Refraction and Dispersion by Immersion," *Jour. Research Nat. Bur. Standards*, **32** [2] 67–75 (1944); RP 1575.

[3] Aniuta Winter, "Time Problem in Annealing," *Jour. Amer. Ceram. Soc.*, **27** [9] 266–74 (1944); p. 267. See also footnote 1.

[4] L. H. Adams and E. D. Williamson, "Annealing of Glass," *Jour. Franklin Inst.*, **190** [6] 597–631 (1920).

[5] N. W. Taylor, "Law of Annealing of Glass, Quantitative Treatment and Theoretical Interpretation," *Jour. Amer. Ceram. Soc.*, **21** [3] 85–89 (1938).

TABLE I

SUMMARY OF INDICES RESULTING FROM VARIOUS HEATING INTERVALS AT TEMPERATURES FROM 914° TO 1060°F.

(1) At 914°F.		(2) At 940°F.		(3) At 960°F.		(4) At 980°F.		(5) At 1000°F.		(6) At 1020°F.		(7) At 1040°F.		(8) 1060°F.	
Hr.	Index	Hr.	Index	Hr.	Index	Minutes	Index	Minutes	Index	Minutes	Index	Minutes	Index	Minutes	Index
0	1.51009	0	1.50978	0	1.50919	0	1.50977	0	1.51003	0	1.50950	0	1.50945	0	1.50961
3	1.51202	6.5	1.51380	0.33	1.51183	25	1.51238	5	1.51185	1.1	1.51115	2	1.51176	2	1.51198
5	1.51253	21.2	1.51468	0.67	1.51226	60	1.51309	30	1.51310	3	1.51195	5	1.51240	4	1.51241
22	1.51351	30.8	1.51500	1.0	1.51249	120	1.51369	60	1.51362	6	1.51247	10	1.51287	6	1.51263
67	1.51411	38.8	1.51515	17.5	1.51474	160	1.51390	90	1.51393	10	1.51287	20	1.51328	8	1.51283
72	1.51424	46.5	1.51526	23.0	1.51518	240	1.51422	120	1.51413	21.4	1.51336	40	1.51350	10	1.51293
88	1.51430	61.5	1.51541	47.1	1.51556	300	1.51438	150	1.51426	40	1.51372			12	1.51299
110	1.51450	68.9	1.51556	63.0	1.51566	363	1.51450	180	1.51438	70	1.51399			15	1.51305
134	1.51466	83.7	1.51565	103.0	1.51577	423	1.51466	210	1.51446	100	1.51412			20	1.51311
235	1.51520	85.2	1.51569			500	1.51479	240	1.51456						
258	1.51524	100.0	1.51577			610	1.51487	270	1.51459						
278	1.51523	118.0	1.51585			700	1.51498								
347	1.51541	132.8	1.51590			800	1.51507								
392	1.51559	155.1	1.51596			900	1.51514								
654	1.51604	169.9	1.51601												
750	1.51625	184.9	1.51603												

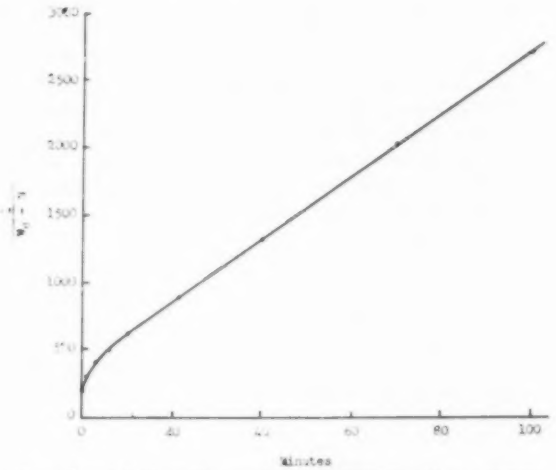

FIG. 3.—$1/(N_s - N)$ vs. time at 1020°F.; $N_s = 1.51448$.

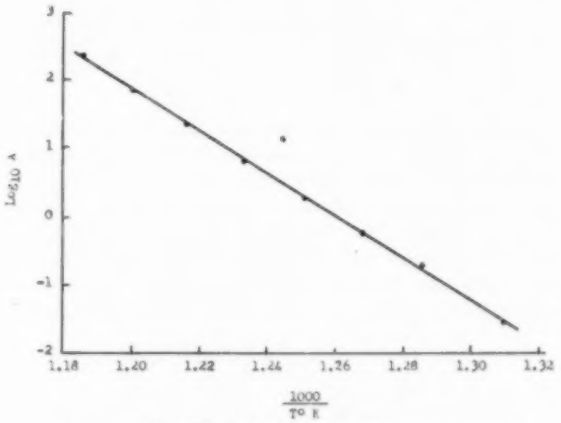

FIG. 4.—Variation of A with absolute temperature.

Table II shows that the rate, A, increases rapidly with temperature. Figure 4 shows that the variation of A with temperature is well expressed by the empirical equation (2).

$$\text{Log } A = K/T + C \qquad (2)$$

T = absolute temp.
K and C = constants.

TABLE II

GRAPHICALLY DETERMINED VALUES OF N_s AND A

Temp. (°F.)	N_s	A/min.
914	1.51670	0.028
940	1.51640	0.211
960	1.51603	0.620
980	1.51560	1.82
1000	1.51505	6.50
1020	1.51448	23.0
1040	1.51383	73.3
1060	1.51335	200.0

VI. Applications

The principal results of this study are equations (1) and (2) and the N_s values for each temperature. In a practical application to annealing, this information can be used to calculate the time that must be spent at each temperature to reach a suitably high index with the shortest annealing cycle. It is sometimes more important to have a uniform index without necessarily reaching the highest value. Here, again, these data are useful in developing such a cycle.

The best annealing cycle to use in any given application must also take into account the release of strain and furnace characteristics. Because of these other factors that must be considered, a general procedure for developing the best index annealing cycle has not been worked out. Compromise cycles based on the foregoing data, however, have been developed and applied to commercial practice with good results. The new cycles yield indices 0.0003 to 0.0010 higher than previous practice and are designed to give a highly uniform index throughout each piece of glass.

TABLE III

EXPERIMENTAL VALUES OF N_s

Temp. (°F.)	N_s	Temp. (°F.)	N_s
1060	1.51326	1140	1.51066
1080	1.51250	1160	1.51027
1100	1.51187	1180	1.50997
1120	1.51119		

VII. Theoretical Value

These equations are also important from a theoretical point of view. Equation (1) has the form of a second-order reaction equation in physical chemistry and equation (2) has the form of the Arrhenius equation for change of reaction rate with temperature. The constant K of equation (2) can be determined from the slope of Fig. 4, and from K the activation energy is found to be 139,000 calories per Avogadro's number of elementary processes. This activation energy is of the same order of magnitude as those derived by Taylor[5] and Taylor and Dear[6] from the rate of strain release, viscosity, and delayed elastic effects of other glasses.

TABLE IV

DECREASING INDICES OF WELL-ANNEALED GLASS AT 1060°F.

Minutes	Index	Minutes	Index
0	1.51620	30	1.51410
4	1.51595	35	1.51392
10	1.51556	40	1.51375
15	1.51522	45	1.51360
21	1.51470	50	1.51349
25	1.51445		

In addition to the data given previously, all of which concern the increasing index of poorly annealed glass, the decreasing index of a well-annealed glass at 1060°F. was studied. The indices resulting from various heating intervals are given in Table IV. The decreasing index follows very closely the form of a first-order reaction in the presence of a second-order counter reaction as shown by Fig. 5, which is a graph of equation (3).

$$\text{Log}\frac{a-(N-N_e)}{N-N_e} = bt + c \qquad (3)$$

a, b, and c = constants.
N_e = 1.51326 (as found by prolonged heating of sample at 1060°F.).

The constant, $a = 0.004$, was chosen to give the most nearly straight line.

It might be expected by analogy that the increasing index of a poorly annealed glass would follow the form of a second-order reaction in the presence of a first-order counter reaction; the corresponding equation would be that of equation (4).

$$\text{Log}\frac{a'+(N_e-N)}{N_e-N} = b't + c' \qquad (4)$$

$a' = a$ of equation (3) if same molecules were involved.

[6] N. W. Taylor and P. S. Dear, "Elastic and Viscous Properties of Several Soda-Silica Glasses in Annealing Range of Temperature," *Jour. Amer. Ceram. Soc.*, **20** [9] 296–304 (1937).

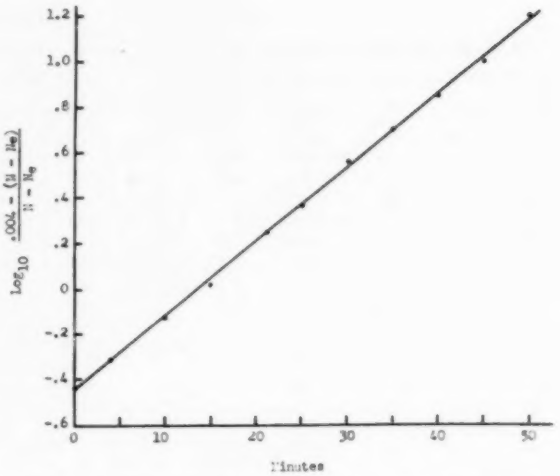

FIG. 5.—Decreasing index at 1060°F.; $N_e = 1.51326$.

When the data of Table I (column (8)) are plotted according to equation (4) with $a' = a = 0.004$ and $N_e = 1.51326$, the agreement is very poor. The molecular transformation manifested by changing index, therefore, must be more complex than the simultaneous first- and second-order reactions dealt with hitherto in physical chemistry.

The data in column (8), Table I, can be well expressed by equation (4) if $a' = 0.0001$ and $N_e = 1.51326$, but equation (1) is preferred for the purposes of this study when N_e is not known and is to be determined graphically. As stated previously, the graphically and experimentally determined values of N_e at 1060° differed by only 0.00009.

VIII. Summary

It has been found that the manner in which the low refractive index of rapidly cooled glass increases during annealing is well expressed by two empirical equations. The equilibrium indices increased from 1.50997 at 1180°F. to 1.51670 at 914°F. for the borosilicate glass studied. The data have been successfully applied to commercial practice.

Theoretical analysis of the data shows that the molecular reaction which causes the index to vary is not of the familiar, simultaneous, first- and second-order type.

LIBBEY-OWENS-FORD GLASS COMPANY
ROSSFORD, OHIO

SOFTENING POINT OF GLASS BY FIBER ELONGATION METHOD AND IMPROVEMENTS IN APPARATUS AND PROCEDURE*

By Arthur H. Falter

Abstract

Detail and assembly illustrations show how the apparatus has been redesigned to maintain a constant rate of heat transmission. A description of the comparator telescope and the method of use is given. Individual curves show the results of softening-point tests on glasses over a range of 260°C., in which the agreement for five individual homogeneous glass specimens varies from 1° to 6°C. when the ordinary portable potentiometer is used. When the glass contains stones or is devitrified, the results are more widely divergent. Uniformity of specimen diameter has a slight effect on the results.

I. Introduction

Glass technologists have evolved, over a period of years, two methods by which the softening temperature of glass can be determined. The interferometer method used by the National Bureau of Standards[1] embraces the determination of thermal expansion, critical temperature, and annealing range in addition to the softening point, all in one operation. Although this method requires a high degree of technical and mechanical skill, it is used in many industrial laboratories.

Littleton[2] has shown that the softening temperature of glass can be determined by observing the tip of a suspended test fiber whose upper portion is heated at a uniform rate of 5° to 10°C. per minute. He defines the softening point of glass[3] as that temperature at which a uniform thread of glass 23.5 cm. long, of a diameter between 0.55 and 0.75 mm., suspended vertically in a furnace of specified characteristics, will elongate under its own weight at the rate of 1 mm. per minute. At that instant, the glass has a viscosity[4] of approximately $10^{7.6}$ poises. Littleton's definition and method have gained considerable acceptance and were the basis for work in 1937 by Wessels,[5] who used a modified apparatus to determine the softening temperatures of glasses containing baryta additions. Although no individual test results are given, it is doubtful whether his modifications improved the accuracy of the apparatus. The next real contribution came in 1940 when Littleton[3] announced the use of a comparator telescope for observing the tip of the specimen. This improvement eliminated the inaccuracies inherent in following the tip of the specimen past a millimeter-scale background.

The present work was undertaken in order to improve the performance of the apparatus and to prove the utility of Littleton's method over a wide range of temperatures and glass conditions.

During the course of the tests, the question arose as

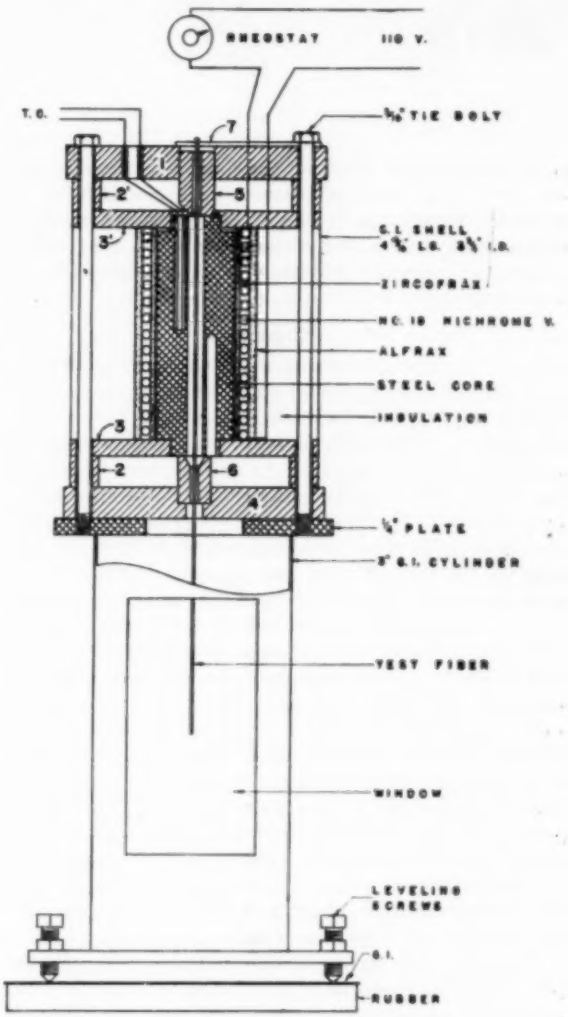

Fig. 1.—Softening-point furnace.

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Glass Division); not listed on Meeting Program. Received April 18, 1944.

[1] J. B. Saunders, "Improved Interferometric Procedure with Applications to Expansion Measurements," *Jour. Research Nat. Bur. Standards*, **23** [1] 179–95 (1939); RP 1227; *Ceram. Abs.*, **18** [11] 206 (1939).

[2] J. T. Littleton, "Method for Measuring Softening Temperature of Glasses," *Jour. Amer. Ceram. Soc.*, **10** [4] 259–63 (1927).

[3] J. T. Littleton, "Softening Point of Glass," *Jour. Soc. Glass Tech.*, **24**, 176–85 (1940).

[4] H. R. Lillie, "Viscosity of Glass Between Strain Point and Melting Temperature," *Jour. Amer. Ceram. Soc.*, **14** [7] 502–11 (1931).

[5] V. F. Wessels, "Effect of Replacing Dolomitic Lime by Baryta on Some Properties of Glass," *ibid.*, **20** [3] 79–84 (1937).

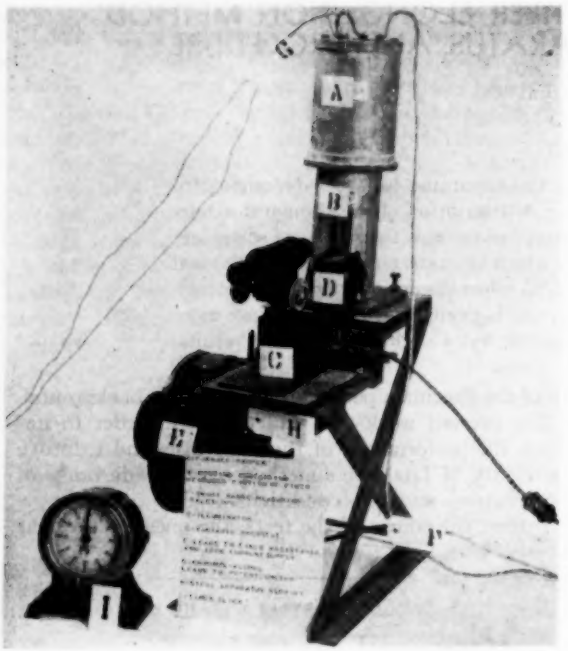

FIG. 2.—Softening-point apparatus assembly.

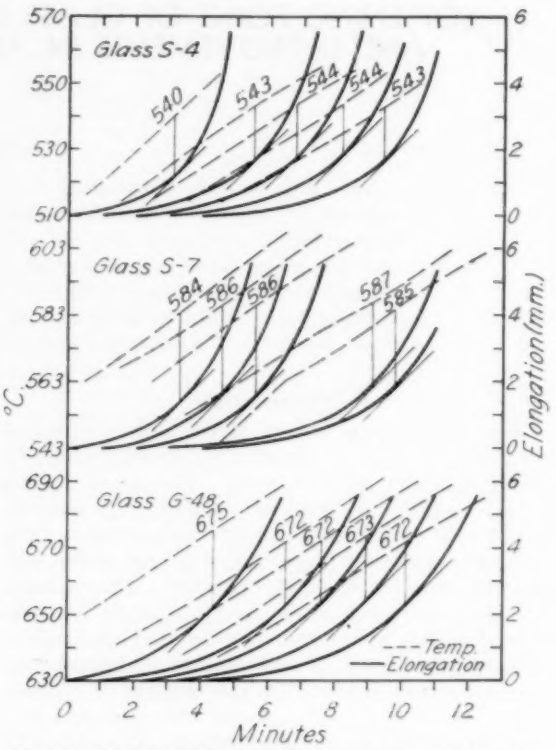

FIG. 3.—Individual tests on homogeneous specimens; samples Nos. S–4, S–7, and G–48.

to the effect on the results if the specimens should vary over the entire range of permissible size tolerances as set up by Littleton and others. This question, together with a study of the effect of "stones" on the test results, constituted a special problem having a bearing on the larger issue.

II. Apparatus

Figure 1 shows the furnace with the upper part in cross section. The central core, which transmits the heat to the test fiber, is made of U.S.S. 12 Z substandard steel. A thin-walled section of Zircofrax combustion tubing fits closely around the steel core. This tube acts as a spool for the helically wound coil composed of 50 ft. of No. 18 Nichrome V wire. The nested arrangement is completed by the Alfrax furnace tube which confines the spirally wrapped heating coil. Parts 3 and 3′ provide support for the core and the surrounding tubes and contain equally spaced holes to permit the insulation of sifted Georgia kaolin to penetrate the inside portions where insulation is desired. Parts 1 to 6, inclusive, are made of Transite; the hanger strip, No. 7, is metal; and Chromel-Alumel thermocouple wires continue outside the furnace to the potentiometer binding posts. A leveling device is provided in order to prevent any part of the test fiber from becoming "hung up" inside parts 5 or 6. Ordinary building vibrations are absorbed by pads of sponge rubber, such as those upon which the furnace rests. The transparent window over the measured portion of the test fiber prevents stray air currents from affecting the results.

Figure 2 shows the apparatus complete except for the portable L & N potentiometer. The variable rheostat is of such capacity as to permit close control of the rate of temperature rise. The short-range measuring telescope was adapted especially for the job. It consists of a simple body tube with a 4x Huyghenian eyepiece and a 3-power objective having a working distance of 95 mm. A micrometer disk scale, contained in the eyepiece, is divided into 100 equal parts; upon calibration, it was found to measure a total elongation of 5.56 mm.

III. Test Methods

To avoid contamination, the glasses were melted in Zircofrax crucibles. The use of this material had an additional advantage in that the filled crucibles could be placed directly into a Globar furnace at a temperature of 1250° to 1400°C., after having been preheated to about 200°. After one hour at the melting temperature, the crucible was withdrawn and allowed to cool until the glass was at the desired working viscosity. Then, by proper manipulation, a glass fiber over 40 ft. in length was drawn from a gather of the glass on the end of a scored tool steel rod. Test fibers were then prepared from those portions which fell within the size tolerances. To provide a ball-bearing contact with the hanger strip, a spherical bead was melted on one end of each test fiber. Blackening of the other end facilitated telescopic observations. When a telescopic device is used to follow the elongation, it must be carefully adjusted for parallax before each observation.

After the furnace had reached the required starting temperature, the fiber was inserted, the telescope adjusted, and the fiber allowed to elongate 3 to 14 divisions, depending on the rapidity of elongation. The tip was then returned to zero, and the readings were

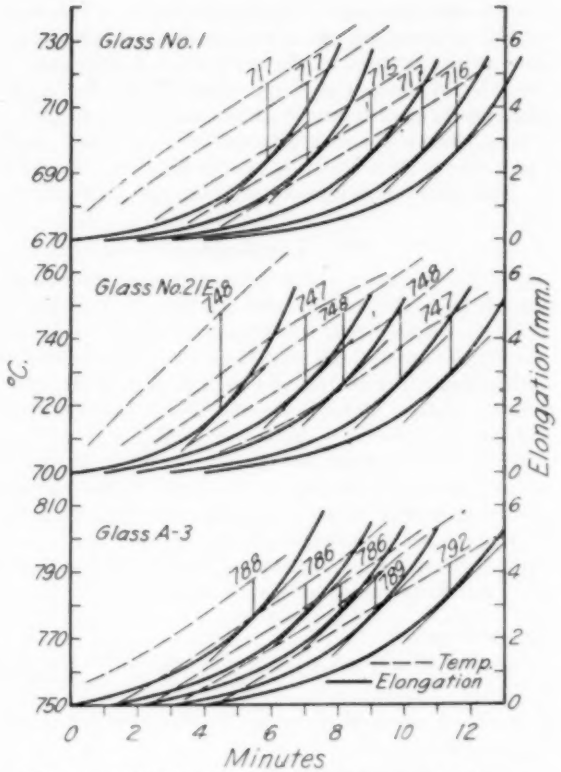

FIG. 4.—Individual tests on homogeneous specimens; samples Nos. 1, 21E, and A–3.

started. It was found that elongation readings every minute and temperature readings every two minutes on the half minute provide sufficient accuracy so that all elongation points fall on a smooth curve. The softening temperature of the fiber was found by projecting the point of 45-degree tangency to the elongation curve up to the time-temperature curve. By moving the time zero point, a number of curves were plotted having the same temperature axis.

Ordinarily, the specimen diameter, from fiber to fiber, was gauged to fall between 0.55 and 0.75 mm. In order to study the effect of diameter variations on the test results, a selection of specimens was made so that five varied in diameter between 0.70 and 0.74 mm. and weighed from 0.251 to 0.262 gm. Another group of five varied in diameter between 0.55 and 0.75 mm. and weighed from 0.166 to 0.235 gm. The latter group was thus about six times more variable in weight and diameter than the former. It should be pointed out, however, that the diameter tolerance of 0.55 to 0.75 mm. was used for all other tests. By running samples of a standard glass after every fifty determinations, a check on the furnace calibration was maintained.

IV. Results

Several examinations of the furnace were made during the period of more than two years when the tests were being run. The original Transite spacers and supports are still being used, and the sifted kaolin insulation has maintained its loose powdery condition in spite

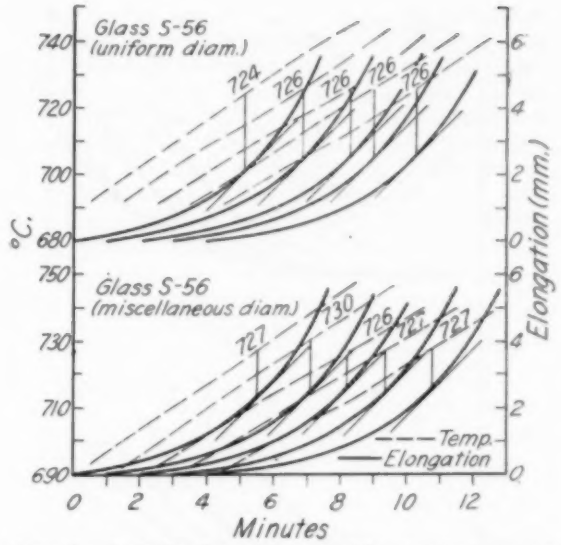

FIG. 5.—Individual tests on sized homogeneous specimens; samples No. S–56, uniform diameter, and No. S–56, miscellaneous diameter.

of a working temperature as high as 1100°C. At this temperature, neither the Nichrome winding nor the steel core has appreciably deteriorated. Both of the refractory tubes are being used well under their recommended limits.

Figures 3 and 4 represent the results of softening-point tests on homogeneous well-melted glasses. The effect of using uniformly sized specimens is illustrated in Fig. 5. Figure 6 shows how incomplete melting or devitrification affects the results.

V. Discussion

The use of Sil-O-Cel has been found generally unsatisfactory at temperatures as high as 1100°C. It tends to harden and contract, which fact alone probably accounts for the changes in heat transmission that other investigators have noted. Because the refractory parts of the furnace are not affected in the present setup, the performance of the apparatus depends on the treatment given the metallic parts, that is, the Nichrome winding, the nickel steel core, and the Chromel-Alumel thermocouple.

Referring again to Figs. 3 and 4, the results on individual specimens show close agreement within each group. Slight differences in heating rate are shown to exist within each group of curves. This difference, however, does not seem to reflect on the uniformity of the individual results. The high-temperature group, represented by glass No. A–3, diverge more widely, but this is believed to be due to the mechanical difficulty of preparing uniform fibers. Figure 5 substantiates this belief. Four of the results on the uniform-diameter specimens are identical; the fifth differs only by two degrees. Contrast this with the results on the variable-diameter specimens where the difference between the extremes is twice as great. The average softening temperature of the samples having uniformly large diameter, moreover, is 2° lower than that of the variable-diameter specimens.

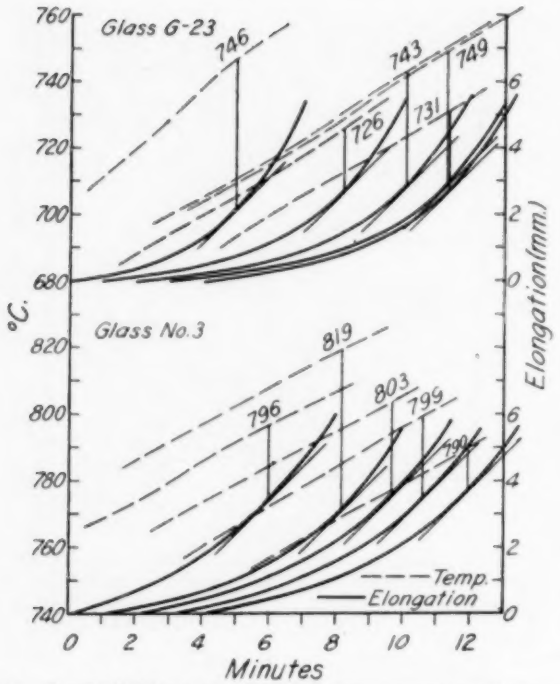

FIG. 6.—Individual tests on nonhomogeneous specimens; samples No. G–23 and No. 3.

When a glass containing "stones" of undissolved matter, such as G–23, is tested, a wide difference in the individual results exists as shown in Fig. 6. A difference of 23°C. between the extremes of individual tests occurs here, although three of the tests show a difference of only 6°. In the case of the devitrified glass No. 3, the difference is even more startling, amounting to 29°C., although three of the results are only 7° apart. Both sets of curves then illustrate the unreliability of softening-point determinations on anything but homogeneous glass.

VI. Conclusions

(1) The accuracy of the softening-point determinations depends on the ability of the furnace to duplicate its over-all rate of heat transmission.

(2) The design of the furnace is such that reasonable duplication of results can be expected in tests on homogeneous glasses having softening points between 540° and 800°C.

(3) The homogeneity of the glass being investigated has an important bearing on the agreement of the test results. Conversely, when the glass is nonhomogeneous, the test results are widely variable.

(4) Uniformity of specimen diameter has a slight effect on the agreement of test results.

Acknowledgment

Grateful acknowledgment is due W. C. Taylor and Evan J. Lewis of Corning Glass Works and to the members of the Carborundum Company research staff who aided in the development of this paper by their help and advice.

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LEWIS ACID-BASE THEORY APPLIED TO GLASS*

BY KUAN-HAN SUN AND ALEXANDER SILVERMAN†

ABSTRACT

According to the Lewis theory of acids and bases, glass formers, such as SiO_2, B_2O_3, P_2O_5, BeF_2, GeS_2, etc., may be classified as acids because they are electron-pair acceptors in glass reactions and the modifiers, Na_2O, CaO, NaF, Na_2S, etc., are bases because they are electron-pair donors; Al_2O_3, Fe_2O_3, BeO, MgO, ZnO, etc., the intermediates, may be classified as amphoteric.

I. Introduction

Conservative individuals usually are slow to accept new theories. In applying a new theory, old concepts must be reshaped or re-formed. This readjustment may be difficult. Take the old oxidation-reduction theory as an example. The idea of oxygen transfer was so convenient and deep rooted to chemists of former times that they did not care to think in terms of the newer electron-transfer theory even though they may have realized that the new theory was better. New theories are not necessarily better, but they should not be ignored simply because of a troublesome readjustment. If the new theories are better, there is every reason for keeping up to date and applying them.

Glass chemists and technologists for years have applied the terms "acidic" and "basic" components to glassmaking substances, but they are fully aware of the fact that there are no hydrogen or hydroxyl ions in glass, using for the moment the terms of the old concepts of acids and bases. In terms of the newer Brönsted proton-transfer theory, when an "acidic-component," such as SiO_2, is fused together with a "basic-component," such as Na_2O, there are no proton transfers. Glass reactions cannot be interpreted by the classical theory or the Brönsted theory of acids and bases although glass chemists and technologists still use the terms "acidic" and "basic" in discussing

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batch or glass ingredients. A new definition of acids and bases is more necessary in glass technology than in pure chemistry.

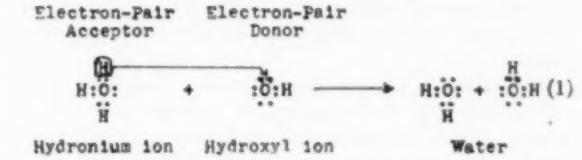
Lewis[1] in 1923 summarized his electron theory of the structure of matter and fifteen years later used this theory to explain the behavior of acids and bases.[2]

II. Review of Acid and Base Theories

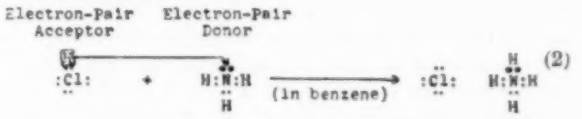
A brief review of the development of acid and base theories may be helpful. According to history, Antoine Lavoisier claimed that all acids contained oxygen.[3] This theory became invalid when Sir Humphrey Davy proved that some acids do not contain oxygen and that many oxides are not even acid-forming. Justus von Liebig then defined an acid as a substance which contains easily replaceable hydrogen atoms. After Svante Arrhenius proposed his theory of ionization, it was generally accepted that an acid is a hydrogen compound which yields hydrogen ions in water; a base is a compound which yields hydroxyl ions in water, and neutralization is the combination of hydrogen and hydroxyl ions to form water. Difficulty is encountered in such reactions as dry HCl and NH_3 in benzene solution, where there are no hydrogen and hydroxyl ions, and also in reactions occurring in pure ammonia, anhydrous acids like hydrofluoric, acetic, etc., and in other solvents. Two theories have been advanced to cover these cases, (1) the theory of solvent systems and (2) the Brönsted theory. The latter, which is more prominent, states that an acid is a proton donor and a base a proton acceptor. Neutralization is just a process of transferring protons. This theory includes many reactions of acids and bases that are not covered in the older theories and has wide application, but it still does not take care of all cases. Neutralization reactions in liquefied sulfur dioxide, phosgene, etc., have no protonic exchange at all. The neutralizing of SiO_2 by Na_2O at high temperatures in glass, moreover, cannot be interpreted by the classical or Brönsted theories. In this and in many other glass reactions, neither the combination of hydrogen and hydroxyl ions nor protonic exchanges are present.

The Lewis theory, which seems to include all known reactions between acids and bases, was then developed.[2] This theory is very simple and easy to learn if all the old concepts of acids and bases are discarded.

According to the Lewis theory, the difference between an acid and a base is not due to the presence of particular atoms or ions but to their differences in electron structure which influences their behavior in the sharing of electrons. In a way it is like oxidation-reduction when this is interpreted through electron rather than oxygen relationships. An acid, accordingly, is an atom, ion, radical, or molecule which can accept an electron pair to form a coordinate bond. A base is an atom, ion, radical, or molecule which can donate an electron pair to form a coordinate bond. Neutralization is the formation of a covalent bond through coordination by an acid and a base. In oxidation-reduction, an oxidizing agent accepts electrons and a reducing agent donates electrons. This action involves the transfer of electrons. The chief difference between neutralization and oxidation-reduction reactions is that the former involves the sharing of electrons to form covalent or coordinate bonds and the latter usually involves the transfer of valence electrons. Reaction (1) illustrates neutralization.

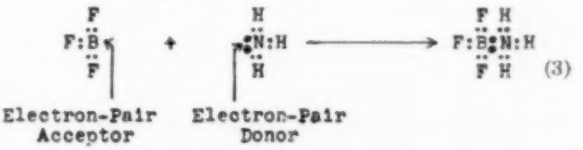


According to the classical theory, the hydrogen ion would have combined with the hydroxyl ion; according to the Brönsted theory, the hydronium ion would have donated a proton to the hydroxyl ion; by the Lewis theory, the hydroxyl ion donates an electron pair to the hydronium ion.



In reaction (2), if HCl donated a proton to NH_3, Brönsted's viewpoint would be fulfilled, but with NH_3 donating an electron pair, as shown, the Lewis theory is illustrated. The classical theory did not provide for a case like this.

Reaction (3) is a typical example of the Lewis theory which has wide application.



In oxidation and reduction, the relative magnitude of electron potentials decides whether a substance should be called an oxidizing or a reducing agent with reference to another substance. The same idea applies to acids and bases but at present only in a qualitative sense. Amphoteric substances occur in the old classical theory, amphiprotic substances in the Brönsted, and amphoteric substances again in the Lewis theory. Water is an amphoteric substance according to the new theory. It is a base toward hydrogen ions, forming hydronium ions; and water is an acid toward ammonia, forming ammonium ions. Whether a substance should be called an acid or a base is not determined by its chemical formula but by its tendency to be an electron-pair acceptor or donor.

III. Lewis Theory Applied to Glass Reactions

Just as a study of nonaqueous solvents at ordinary temperatures has resulted in a reinterpretation and

[1] G. N. Lewis, Valence and Structure of Atoms and Molecules. Chemical Catalog Co., Inc., New York, 1923.

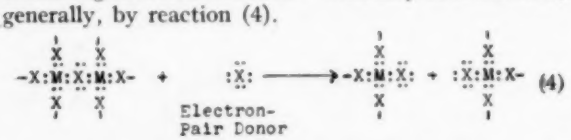
[2] (*a*) G. N. Lewis, "Acids and Bases," *Jour. Franklin Inst.*, **226** [1] 293–313 (1938).
(*b*) W. F. Luder, "Electronic Theory of Acids and Bases," *Chem. Revs.*, **27** [3] 547–83 (1940).

[3] F. J. Moore and W. T. Hall, History of Chemistry. McGraw-Hill Book Co., Inc., New York, 1931.

broader application of acid-base theories, a study of high-temperature nonaqueous reactions will throw more light on the subject. Glass is an inorganic vitreous substance which is not only a nonaqueous solution but also a high-temperature product. Reactions in glass systems should be of particular interest. Audrieth and Moeller[4] have briefly discussed high-temperature neutralization reactions. Stegmaier and Dietzel[5] have studied the basicity of glass in detail. Although they have not applied the Lewis theory, they have extended the idea of using oxygen-ion concentration as a measure of basicity in glass. This idea specifically is in accord with the general application of the Lewis theory to glass, which will be elaborated in the following discussion.

Glass chemists have conveniently classified glass components into three classes as follows: (1) Glass formers, which constitute the backbone of glasses and usually can form a glass alone; SiO_2, B_2O_3, P_2O_5, GeO_2, BeF_2, $ZnCl_2$, GeS_2, etc., are in this class; (2) modifiers, which do not form a glass by themselves but which may be introduced into glass to modify its properties; they usually weaken the glass structure; Na_2O, K_2O, CaO, BaO, NaF, NaCl, Na_2S, etc., belong to this class; and (3) oxides, such as BeO, ZnO, MgO, Al_2O_3, Fe_2O_3, etc., which exert a binding force in glass between the glass formers and the modifiers, called intermediates.

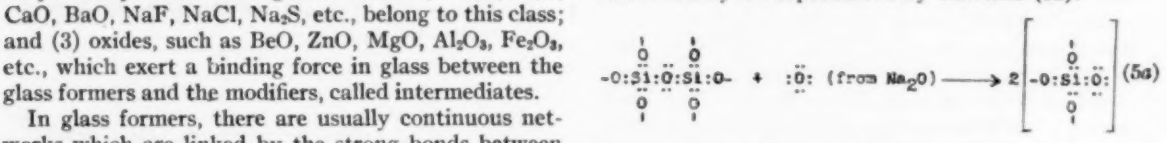
In glass formers, there are usually continuous networks which are linked by the strong bonds between the positive ions of Si, B, P, Ge, etc., and the negative ions of O, F, Cl, S, etc. The positive ions are usually electrophilic and if there is an excess of loosely bonded negative atoms, present or introduced, a rearrangement of ions would be expected or a reaction which results in sharing electrons of these positive ions with the excess negative ions or atoms. This may be illustrated, generally, by reaction (4).



(4)

In equation (4), the glass former, MX_2, reacts as an acid and receives a pair of electrons from the donor, $:\ddot{X}:$, which serves as a base. In equation (4) and other equations in this paper, electronic configurations are given only to those atoms which involve significant changes in the reactions. The single bonds represent the sharing of one pair of electrons with another "M." By means of these single bonds, a continuous network structure of the glass former, MX_2, is indicated. The pair of electrons attached to one of the four "X"s in the reaction products may be loosely shared with several metallic ions derived from the modifiers.

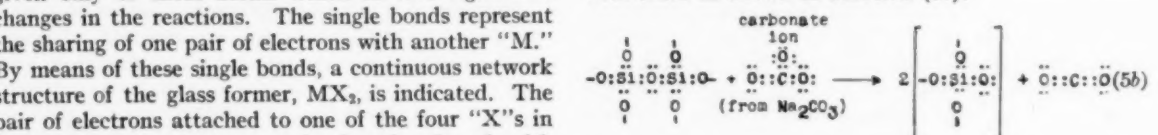
The role of modifier may be cleared by studying the case of fused Na_2O. Crystalline Na_2O is known to have a CaF_2 type of structure in which each sodium is surrounded by four oxygens and each oxygen by eight sodiums.[6] The structure of liquid Na_2O is unknown and is dependent on temperature. In glass, it is known that each sodium is surrounded by six oxygens.[7] For the first approximation, the structure of liquid Na_2O is assumed to be a random and very weak network of sodium and oxygen ions with each sodium surrounded by four, six, or more (or fewer) oxygens according to the temperature. It is impossible, apparently, to draw significant electronic structures for such linkages. One thing is certain, the binding force between any single sodium and oxygen must be very weak, approximately of the order of one thirtieth* of the corresponding silicon-oxygen binding. Such "bonds" or binding forces can therefore be broken very easily. If other stronger positive ions are present, it should be relatively easy for the oxygen ions in Na_2O to form a "bond" with the stronger positive ions. Negative oxygens in the modifiers consequently behave like a base in the Lewis theory because they donate a pair of electrons when they react. A typical glass reaction may be represented by reaction (5*a*).



(5*a*)

This is a typical neutralization reaction. During the reaction, it might be assumed that one of the two bonds between Si–O–Si is broken first. The partially free silicon atom is now capable of accepting a pair of electrons and behaves as an acid. The $:\ddot{O}:$ from modifier-oxides donates the pair and acts as a base. The complete reaction is shown in equation (5*a*). All glass formers should behave more or less like the SiO_2 in equation (5*a*) and all the modifiers should behave like Na_2O. It may, therefore, be stated qualitatively that, according to the Lewis theory, in general, glass formers are acids and modifiers are bases. Intermediates are amphoteric substances. They behave like a base with the glass formers and like an acid with modifiers.

If a glass technologist were asked to name the simplest glass, he would probably say water glass (sodium metasilicate). In its production, sodium carbonate reacts with silica as shown in reaction (5*b*).



(5*b*)

[4] L. F. Audrieth and Therald Moeller, "Acid-Base Relationships at High Temperatures," *Jour. Chem. Education*, **20** [5] 219–22 (1943).

[5] W. Stegmaier and A. Dietzel, "Significance of Basicity of Glass Melts and Investigation of Its Measurements, I–II," *Glastech. Ber.*, **18** [11] 297–308; [12] 353–62 (1940); *Ceram. Abs.*, **20** [10] 235–36 (1941).

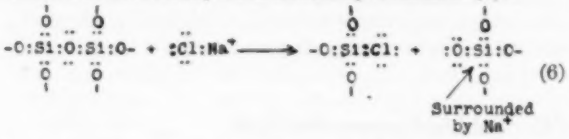
[6] E. Zintl and H. H. v. Baumbach, "Über Natriumoxyd," *Z. Anorg. Allgem. Chem.*, **198** [1] 88–101 (1931); *Ceram. Abs.*, **10** [9] 665 (1931).

[7] B. E. Warren, "X-Ray Diffraction Study of Structure of Glass," *Chem. Revs.*, **26** [2] 237–55 (1940); *Ceram. Abs.* **19** [8] 187 (1940).

* This very approximate estimation was made on the assumption that the binding force is directly proportional to the valence of the cation and inversely proportional to the square of the interionic distance, M–O, and to the coordination number of oxygen.

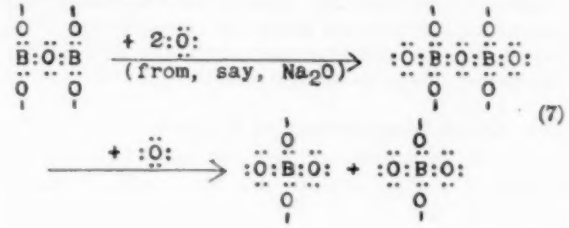
In reaction (5*b*), one of the two $:\ddot{O}:$ of the carbonate ion might, in a sense, be looked upon as an ion of itself, which as a base donates a pair of electrons to the acid.

An interesting reaction might be cited which could never be considered a neutralization reaction on the basis of the old classical theory. The introduction of metallic halogenides, such as KF, NaCl, etc., into silicate or borate glasses is well known. These reactions can be satisfactorily illustrated by reaction (6).



(6)

It is interesting to note that the alkali halogenides, typical salts under the classical theory, act as bases in glass reactions.



(7)

The well-known change of coordination of boron from three to four in glass is also a typical neutralization reaction according to the Lewis theory in reaction (7). It is apparent from these equations that B_2O_3 is an acid in a double sense. This explains why B_2O_3 is considered a strong acid by the glass technologists even though its aqueous solution is a rather weak acid.

IV. Conclusion

Although Lewis offers the most inclusive theory for acids and bases, it is by no means quantitative. In this respect, the modern ion-electron theory of oxidation and reduction is one step ahead. This theory gives the measurement of oxidation-reduction potentials as a quantitative guide. A list of relative bond strengths in all glass-forming components would be useful for the quantitative interpretations of acid-base reactions in glass.

Acknowledgment

The authors gratefully acknowledge suggestions from Maurice L. Huggins concerning some of the theoretical aspects of this paper.

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SOME PROPERTIES OF SODA-SILICA GLASSES AT HIGH TEMPERATURES*

By Kuan-Han Sun† and Hurd W. Safford

Abstract

A study is made of density, expansion, surface tension, parachor, and viscosity data for glasses in the system Na_2O–SiO_2 within the temperature range 900° to 1400°C. The best values have been selected and correlated with composition.

I. Density and Expansion

In the consideration of a particular system, variables are usually encountered such as T (temperature), V (volume), P (pressure), and C (concentration). At ordinary conditions of temperature and pressure, a discussion of density involves but two variables, V and C. When density at various temperatures or thermal expansion is under consideration, a third variable, T, must be considered.

The methods for determining density and thermal expansion below the softening point of glass are but slightly related. Above the softening point, density and thermal-expansion data usually result from the same experimental source; thus, a measurement of the volume of glass at different temperatures will give such information.

There have been but few systematic and accurate studies of volume measurements for all types of glass at high temperatures. In addition to those reviewed by Morey,[1] investigations of this nature have been carried out by Jaeger,[2] Endell and Wens,[3] Volarovich and Leont'eva,[4a] Badger and Harman,[5] Ellefson and Taylor,[6] Parmelee, Lyon, and Harman,[7] Sawei and Inoue,[8] and Scholes and Mooney.[9] A brief summary of the methods used by various investigators follows.

* Presented by N. W. Taylor at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 21, 1942 (Glass Division). Received May 26, 1944.

Contribution No. 490, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

† Now at Research Laboratories, Eastman Kodak Company, Rochester, N. Y.

[1] G. W. Morey, Properties of Glass, pp. 259–61, 272. American Chemical Society Monograph Series, Reinhold Publishing Corp., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48 (1939).

[2] F. M. Jaeger, "Über die Temperaturabhängigkeit der molekularen freien Oberflachenenergie von Flüssigkeiten im Temperaturbereich von −80 bis +1650°C.," *Z. Anorg. Allgem. Chem.*, **101**, 1–214 (1917).

[3] Kurd Endell and C. Wens, "Über Beziehungen zwischen Dichte Flüssigeitsgred und Schamottsteinangriff von Gläsern und Schlacken bei hohen Temperaturen," *Glastech. Ber.*, **13** [3] 78–86 (1935); *Ceram. Abs.*, **15** [1] 15 (1936).

* Footnotes 4–9 on page 12.

(1) Flotation Method

This method is similar to the flotation method used in the determination of density at ordinary temperatures except that molten salts are employed as flotation media. This procedure as reviewed by Day, Sosman, and Hostetter [10] has become obsolete, and the early results were not consistent.

(2) Methods Involving Archimedes' Principle

(*A*) *Weighing Glass in Liquid:* (i) Using liquid metal as the immersion medium: This was the method employed by Day, Sosman, and Hostetter in which molten tin was used as the buoyant liquid with the sample submerged under an inverted graphite bell. The buoyant force exerted by the sample on the graphite bell was directly balanced by weights.

(ii) Using such molten salts as LiCl, NaCl, and KCl as the buoyant media: The sample is usually placed in a platinum vessel and the whole is weighed while immersed in molten salts. This procedure was extensively used by Hänlein,[11] Endell and Wens[3] Heidkamp and Endell,[12] Sawei and Inoue,[8] and others.

(*B*) *Weighing Metal Weight, Usually Platinum or Platinum Alloy, in Molten Glass:* If the coefficient of thermal expansion of the metal used is known, the density of the glass can be determined easily. This method has been followed by Jaeger,[2] Li,[13] and Parmelee and Lyon.[14]

(3) Method Based on Stokes' Law

The speed of a moving spherical body in a viscous liquid depends on the radius and density of the body and the viscosity and density of the liquid. By using a platinum ball immersed in glass, Sawei and Inoue[15] were able to determine the density of glass by observing the rate of motion of a platinum ball with a balancing device.

(4) Bubble-Pressure Method

For a given liquid at a given temperature, the pressure of a bubble blown from a platinum capillary immersed in molten glass is a function of the depth of the capillary tube and the density of the liquid. By measuring the pressure difference at two levels of the liquid, Badger and Harman[5] were thus able to calculate the density of molten glass.

(5) Direct Measurement of Volume

Density is weight per unit volume. Although the weight of a glass can be very easily and accurately measured when the specimen is at room temperature, its volume at certain temperatures is often difficult to determine. The volume of a given amount of glass at high temperatures may be measured in two ways, (*A*) and (*B*), as follows:

(*A*) *Sessile-Drop Method:* The shape of a drop of glass resting on a flat surface such as graphite can be photographically recorded, and by a suitable mathematical treatment of its dimensional values, the volume may be calculated. Ellefson and Taylor[6] have applied the method to some simple glasses but reported an accuracy of only 5 to 10%.

(*B*) *Platinum Test Tube:* Volarovich and Leont'eva[4] and Volarovich[16] have used a platinum test tube of definite dimensions, and by observing the height of liquid glass in the tube, they were able to deduce the volume of the glass. The height of the glass level was measured by an electrical contact device attached to a micrometer.

The densities of certain molten soda-silica glasses

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[4] (*a*) M. P. Volarovich and A. A. Leont'eva, "Bestimmung des spezifischen Volumens von Schmelzen bei Temperaturen bis 1400," *Z. Anorg. Allgem. Chem.*, **225**, 327–32 (1935).

(*b*) M. P. Volarovich and A. A. Leont'eva, "Specific Volume of Fused Salts at High Temperatures," *Compt. Rend. Acad. Sci., U.R.S.S.*, **2**, 539–41 (1935); in German, p. 542.

[5] A. E. Badger and C. G. Harman, "Determining Density of Molten Glasses," *Glass. Ind.*, **19** [4] 145 (1938); *Ceram. Abs.*, **18** [3] 71 (1939).

[6] B. S. Ellefson and N. W. Taylor, "Surface Properties of Fused Salts and Glasses: I, Sessile-Drop Method for Determining Surface Tension and Density of Viscous Liquids at High Temperatures," *Jour. Amer. Ceram. Soc.*, **21** [6] 193–205 (1938).

[7] C. W. Parmelee, K. C. Lyon, and C. G. Harman, "Surface Tensions of Molten Glass," *Univ. of Ill. Eng. Expt. Station Bull.*, No. 311, 50 pp. (1939); *Ceram. Abs.*, **18** [11] 295 (1939).

[8] I. Sawei and S. Inoue, "Specific Gravity of CaO–Na_2O–SiO_2 Glasses at High Temperatures, I–XVIII," *Jour. Soc. Chem. Ind., Japan*, **40** [7] 198–200B (1937); **41** [10] 337–39B; [12] 846–49 (407–408B) (1938); **42** [5] 286–89 (160–61B); [10] 699–701, 701–703, 703–704 (331–32B); [12] 881–84 (407–409B) (1939); **43** [2] 84–95 (47–49B); [8] 241–43B, 243–45B; [10] 325–28B (1940); this series of articles may be found abstracted in the following issues of *Ceram. Abs.*, **17** [5] 181 (1938); **18** [8] 205 (1939); **19** [3] 62–63 (1940); **20** [1] 11–12 (1941); **21** [8] 168; [9] 187–88 (1942).

[9] S. R. Scholes and Kurt Mooney, "Method for Estimating Expansibility of Glass at High Temperatures." Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (not published).

[10] A. L. Day, R. B. Sosman, and J. C. Hostetter, "Determination of Mineral and Rock Densities at High Temperatures," *Amer. Jour. Sci.*, [4th Series], **37**, 1–39 (1914).

[11] W. Hänlein, "Über das spezifische Gewicht von Glas in Abhängigkeit von der Temperatur," *Glastech. Ber.*, **10** [3] 126–30 (1932); *Ceram. Abs.*, **11** [6] 355 (1932).

[12] G. Heidkamp and Kurd Endell, "Über die Abhängigkeit der Dichte und der Zähigkeit von der Temperatur in System Na_2O–SiO_2," *Glastech. Ber.*, **14** [3] 89–103 (1936); translated in *Glass Ind.*, **17** [7] 227–30 (1936); *Ceram. Abs*, **15** [9] 272 (1936).

[13] S. H. Li (thesis, Univ. of Illinois, 1922) cited by E. W. Washburn and E. E. Libman, "Viscosities and Surface Tension of Soda-Lime Glasses at High Temperatures: II, Surface Tension of Glasses at High Temperatures," *Univ. of Ill. Eng. Expt. Station Bull.*, No. 140, pp. 53–71 (1924); extended abstract in *Ceram. Abs.*, **3** [12] 342–44 (1924).

[14] C. W. Parmelee and K. C. Lyon, "Surface Tensions of Molten Glass, I," *Univ. of Ill. Eng. Expt. Station Bull.*, No. 311, pp. 5–27 (1939); *Ceram. Abs.*, **18** [11] 295 (1939).

[15] I. Sawei and S. Inoue, "Spezifisches Gewicht der ternären Gläser CaO–Na_2O–SiO_2 bei hoher Temperatur, IX," *Jour. Soc. Chem. Ind., Japan*, **42**, 407–409B (1939).

[16] M. P. Volarovich, "Investigation of Heat Expansion of System $Na_2B_4O_7$–B_2O_3 in Molten State," *Bull. Acad. Sci. U.R.S.S., Classe Sci. Math. Nat.*, **5**, 663–74 (1935); *Ceram. Abs.*, **13** [5] 112 (1934); also in *Acta Physicochemica, U.R.S.S.*, **2**, 695 (1935).

have been measured by Li,[13] Ellefson and Taylor,[6] and Heidkamp and Endell.[12] Li's values were not consistent and have been disproved by Ellefson and Taylor.[6] The latter, however, reported data only at two different temperatures and their method of measurement was not of high accuracy.

As far as the authors of this paper have been able to judge, the data of Heidkamp and Endell for six Na_2O-SiO_2 glasses (1000° to 1400° C.) are probably the most accurate and comprehensive for this system. These data have been used herein by plotting for each glass its specific volume at various temperatures; for all of the compositions, straight lines were drawn in. That the deviation of the experimental points from the straight lines was within experimental error indicates that the change of specific volume of any glass in the range 40 to 80 weight % of SiO_2 is a linear function of temperature in the range 900° to 1400°C. In other words, the coefficient of thermal expansion, α_v, is constant for a particular composition and its value can be obtained directly by measuring the slope of the line.

The coefficient of cubical expansion can be expressed as shown in equations (1) and (2). The term, α_v, as

$$\alpha'_v = (1/V_t) \cdot dV/dt \quad (1)$$

$$\alpha''_v = (1/V_0) \cdot dV/dt \quad (2)$$

α'_v and α''_v = coeff. of cubical expansion defined by respective equations.
V_t = vol. of glass at temp., t.
V_0 = vol. at arbitrarily chosen temp., usually 0°C. or room temp.

used here, is different from the symbols for the coefficient of cubical expansion and represents the change in specific volume per degree Centigrade, or the change in volume per gram per degree Centigrade. Its relations with α'_v and α''_v can be expressed as shown in equations (3) and (4).

$$\alpha_v = v_t \alpha'_v \quad (3)$$

$$\alpha_v = v_0 \alpha''_v \quad (4)$$

v_t and v_0 = specific vol. at temp. t and 0°C. or room temp., respectively.

Sawei and his associates[5] have measured the densities of soda-lime-silica glasses from room temperature up to about 1400°C. By plotting the specific volumes of certain of their glasses against temperature, two straight lines were obtained for each glass with curve breaks at about 500° to 600°C. In other words, the quantity, α_v, is approximately constant in the two ranges of temperature, room temperature-softening point (500° to 600°C.) and softening point (1400° C.). The slope for the latter range is steeper than that of the former, as would be expected. The constancy of α_v values for these soda-lime-silica glasses prompted the writers to postulate that the slopes of corresponding lines in the Na_2O–SiO_2 system would probably remain constant down to about 600°C. (softening range) if data were available to indicate that fact.

In order to establish equations for the calculation of the specific volume and the coefficient of expansion of soda-silica glasses at high temperatures, the slopes of the straight lines and the specific volumes at 1400°C. for this system were plotted against weight percentages of SiO_2. For such a binary system, a specific volume-weight percentage plot is just as logical as one in which the mole-volume is graphed against the number of moles of one of the components. Huggins[17] has shown that, for all glasses, linear additivity of volume is a function of the "atomic fraction" of silica. The data at high temperatures, however, were not so accurate and comprehensive as those at room temperature, and only an empirical treatment has been employed. The results which permit the calculation of the specific volume at 1400°C. and the coefficient of expansion are shown in additive equations (5) and (6).

$$v_{1400^\circ} = p_S v_S + p_N v_N \quad (5)$$

v_{1400° = specific vol. at 1400°C.
p_S and p_N = weight % of SiO_2 and Na_2O, respectively.
v_S and v_N = respective factors for specific vol.

$$\alpha = p_S \alpha_S + p_N \alpha_N \quad (6)$$

α = coeff. of cubical expansion/gm. glass.
α_S and α_N = expansion factors for SiO_2 and Na_2O, respectively.

TABLE I

SPECIFIC VOLUME (1400°C.) AND EXPANSION FACTORS

Range of composition (% SiO_2)	Specific vol. factors (1400°C.) × 10^2 ml./gm.		Expansion factors × 10^6 ml./ml./gm./°C.	
	v_S	v_N	α_S	α_N
40–50	0.4125	0.5026	−590	1472
50–80	0.4462	0.4689	122	761

For two ranges of composition, namely, 40 to 50% SiO_2 and 50 to 80% SiO_2, factors were evaluated and are listed in Table I.

By combining equations (5) and (6), it is possible to calculate the specific volume at any temperature within the range of 900° to 1400°C. by equation (7).

$$v = p_S[v_S - (1400 - t)\alpha_S] + p_N[v_N - (1400 - t)\alpha_N] \quad (7)$$

v_t = specific vol. at any temp., t.

By substituting suitable constants in equation (7) and using $p_S + p_N = 100$, the simplified equations (8) and (9) for the two ranges of compositions are obtained.

For 40 to 50 weight % of SiO_2,

$$v = 0.2965 + 1.47 \times 10^{-4} t + p_S (1984 - 2.06t)\ 10^{-6} \quad (8)$$

For 50 to 80 weight % of SiO_2,

$$v = 0.3623 + 0.761 \times 10^{-4} t + p_S (667 - 0.637t)\ 10^{-6} \quad (9)$$

Equations (8) and (9) have been used to calculate density values of the Heidkamp and Endell glasses. The average deviation from experimental results is about 0.09%; their experimental error according to these authors is about 1.3%.

The negative expansion factor for SiO_2 in the 40 to 50% SiO_2 range is very interesting and indicates the strong binding nature of SiO_2 when it is added to a glass composition. This binding action is so strong that it causes a negative contribution to expansion, which fits perfectly the modern concept of glass structure.

It is a well-known fact that at room temperature an increase in Na_2O content causes a decrease in the

[17] M. L. Huggins, "Density of Silicate Glasses as Function of Composition," *Jour. Optical Soc. Amer.*, **30**, 420–30 (1940); *Ceram. Abs.*, **20** [2] 41 (1941).

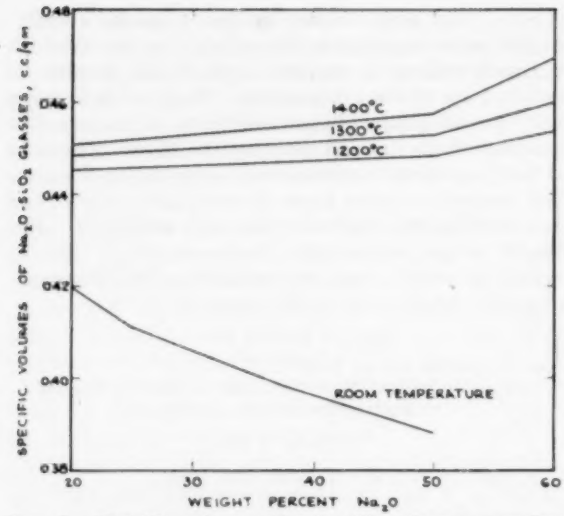

FIG. 1.—Specific volumes of soda-silica glasses at various temperatures.

volume of soda-silica glass.[18] A study of Fig. 1 will reveal that at high temperatures an increase of Na_2O increases the volume of soda-silica glasses. This reversing effect is quite interesting and can be explained from modern theories of glass constitution. At room temperature, the decrease in volume with increase in Na_2O content may be attributed to the fact that Na^+ of Na_2O enters the glass merely by occupying the holes of the SiO_4 network. This contribution to volume is very slight and results in the decrease of volume on substitution of SiO_2 by Na_2O. On the other hand, an increase in Na_2O content usually causes a loosening of the glass structure which results in a glass of high coefficient of expansion. As the temperature rises, the expansion contribution will offset the hole-occupying effect and the volume of glass is increased with increase in Na_2O content.

II. Parachor and Surface Tension

Sugden[19] was the first to suggest and demonstrate that the quantity parachor is an additive function of chemical composition. The parachor, Φ, may be calculated according to equation (10).

$$\Phi = Mv\sigma^{1/4} \qquad (10)$$

M, v, and σ = mol. wt., specific vol., and surface tension of liquid substances, respectively.

The additive nature of parachor for organic substances is well established but for inorganic substances, much improvement is needed.[20] The calculation of parachor for glass systems may be significant and may lead to a better understanding of the structure of glass. It is possible to assign to each glass constituent a parachor factor such that the parachor of glass can be calculated additively just as is the refraction of glass.[21]

For these parachor calculations, the specific volume and surface tension at various temperatures are required. In the soda-silica system, the specific-volume equations (8) and (9) have been shown to be accurate well within the experimental error. Concerning surface-tension data, Morey[1] has stated,

> There is a discrepancy (in surface tension) among the various observers far greater than can be explained by differences in composition or in temperature. The values for silicate glasses range from about 128 to 167 dynes per cm., obtained by Washburn, Shelton, and Williams, to about 400 to 500 dynes per cm., obtained by Lecrenier.

In the last few years, however, the surface-tension data reported by workers in different laboratories using different methods[22] have been in agreement with the 300 dynes per cm. estimated by Morey.

The surface tensions of six soda-silica glasses have been measured at various temperatures (1000° to 1400°C.) by Parmelee, Lyon, and Harman[7], using the bubble-pressure method. Their data are considered reliable and have been used by the authors for the calculation of parachor. Rather than compute a

$$\Phi = \frac{p_S}{100}\left[\Phi_S - (1400 - t) \times 0.000093\right] + \frac{p_N}{100}\left[\Phi_N - (1400 - t) \times 0.000093\right] \qquad (11)$$

Φ = specific parachor of glass.
Φ_S and Φ_N = respective parachor factors at 1400°C. for SiO_2 and Na_2O.

$$\Phi = p_S\left[0.01806 - (1400 - t) \times 93 \times 10^{-8}\right] + p_N\left[0.01968 - (1400 - t) \times 93 \times 10^{-8}\right] \qquad (12)$$

$$\Phi = 1.838 - 0.00162\, p_S + 0.000093\, t.$$

[18] (*a*) K.-H. Sun, H. W. Safford, and Alexander Silverman, "Review of Relation of Density and Refractive Index to Composition of Glass, I," *Jour. Amer. Ceram. Soc.*, **23** [11] 315–26 (1940).
(*b*) J. C. Young, F. W. Glaze, C. A. Faick, and A. N. Finn, "Density of Some Soda-Potash-Silica Glasses as Function of Composition," *Jour. Research Nat. Bur. Standards*, **22** [4] 453–64 (1939); RP 1197; *Ceram. Abs.*, **18** [9] 237 (1939).
See also footnote 17.

[19] S. Sugden, The Parachor and Valency. George Routledge & Sons, Ltd., London, 1930.

[20] See, however, K.-H. Sun and Alexander Silverman, "Parachors and Radii," *Jour. Phys. Chem.*, **47**, [1] 50–59 (1943).

[21] (*a*) M. L. Huggins, "Refractive Index of Silicate Glasses as Function of Composition," *Jour. Optical Soc. Amer.*, **30** [10] 495–504 (1940); *Ceram. Abs.*, **20** [2] 42 (1941).
(*b*) M. L. Huggins, "Silicate Glasses, Calculation of Densities, Refractive Indices, and Dispersions from Glass Compositions," *Ind. Eng. Chem.*, **32** [11] 1433–36 (1940); *Ceram. Abs.*, **20** [2] 42 (1941).
(*c*) M. L. Huggins and K.-H. Sun, "Calculation of Density and Optical Constants of Glass from Its Composition in Weight Percentage," *Jour. Amer. Ceram. Soc.*, **26** [1] 4–11 (1943).
(*d*) J. C. Young and A. N. Finn, "Effect of Composition and Other Factors on Specific Refraction and Dispersion of Glasses," *Jour. Research Nat. Bur. Standards*, **25** [6] 759–82 (1940); RP 1352; *Ceram. Abs.*, **20** [4] 88 (1941).
See also footnote 18.

[22] (*a*) C. L. Babcock, "Surface-Tension Measurements on

molecular parachor, however, the specific parachor, Φ, which may be defined as $\Phi = v\sigma^{1/4}$, was calculated. When specific parachors for the six compositions in the soda-silica system were plotted against temperature, a series of parallel lines with approximately the same slope resulted. A mean value, 0.000093 specific parachor unit per degree Centigrade, was chosen as the temperature coefficient of the specific parachor for all compositions. The specific parachors at 1400°C. were interpolated and plotted against composition (percentage SiO_2). From the resulting straight-line graph, equation (11) was derived. Equation (12) was then obtained by substituting numerical values for the factors and simplifying equation (11).

When the parachors calculated by equation (12) were compared with experimental values, a deviation of about 1% for all the glasses was observed.

The specific parachor factors for SiO_2 and Na_2O at any temperature are $[1.806 - (1400 - t) \times 0.000093]$ and $[1.968 - (1400 - t) \times 0.000093]$, respectively. The corresponding molecular parachor factors, $[108.5 - (1400 - t) \times 0.0056]$ and $[122.0 - (1400 - t) \times 0.0058]$, are obtained by multiplying the specific parachor factors by the respective molecular weights. Molecular parachor factors may be used to calculate the molecular parachor of glass if mole fractions, not weight percentages, are used in the linear addition equation.

As the foregoing outline affords a method of calculating the specific volume and specific parachor of a glass from its composition at any temperature between 900° and 1400°C., it is obvious that the surface tension of the same glass can be readily derived from equation (13).

$$\Phi = v\sigma^{1/4} \qquad \text{or } \sigma = (\Phi/v)^4 \qquad (13)$$

III. Viscosity

Probably the best data on the viscosity of soda-silica glasses are those of Lillie,[23] who measured this property for fifteen glasses in the composition range of 20 to 40 weight % of Na_2O at 800° to 1400°C. From a treatment of his data, it was found that, for each glass, log η (η, the viscosity) bears a better straight-line relationship with $1/t$* (t, temperature in °C.), than with $1/T$ (T, temperature on the absolute scale). The relation shown in equation (14) was obtained for each glass.

$$\text{Log } \eta = A + b/t \qquad (14)$$

a and b = constants found to bear approx. linear relation with composition expressed either in weight or mole %.

From these considerations, the authors obtained equations (15) and (16), by which calculations of viscosity from composition may be made at any temperature in the range 800° to 1400°C.

$$\text{Log } \eta_t = 0.0167p_S - 3.548 + \frac{1}{t}(2658 + 43.55p_S) \qquad (15)$$

$$\text{Log } \eta_t = 0.01775X_S - 3.632 + \frac{1}{t}(2320 + 43.8X_S) \qquad (16)$$

p_S and X_S = weight and mole % of SiO_2, respectively.

Since the original derivation of equations (15) and (16), the writers have discovered a better treatment, which is more sound theoretically and will fit data empirically in a better fashion. This investigation is under way and will be reported in a later paper.

It is to be noted that by combining equations (12) and (15), a composition-independent equation may be obtained which will involve only surface tension, viscosity, density, and temperature. Such an equation will be forthcoming after the improved viscosity relationship has been further tested.

IV. Summary

The best density, surface-tension, and viscosity data for Na_2O-SiO_2 glasses at high temperatures (900° to 1400°C.) have been studied and correlated with composition. The following relationships result:

(*A*) *Expansion:* (i) For 40 to 50% of SiO_2, $\alpha \times 10^9 = -590p_S + 1472p_N$; (ii) For 50 to 80% of SiO_2, $\alpha \times 10^9 = 122p_S + 761p_N$, where α = coefficient of cubical thermal expansion/gm. glass/°C., p_S = wt. % SiO_2, and p_N = wt. % Na_2O.

(*B*) *Specific Volume (Reciprocal of Density):* (i) For 40 to 50% of SiO_2, $v_t = 0.2965 + 1.47 \times 10^{-4}t + (1984 - 2.06t) \times 10^{-6}p_S$; (ii) For 50 to 80 % of SiO_2, $v_t = 0.3623 + 0.761 \times 10^{-4}t + (667 - 0.637t) \times 10^{-6}p_S$; where v_t = specific vol. of glass at temperature, t, and t = temp. °C.

(*C*) *Parachor and Surface Tension:* For 60 to 80% of SiO_2, specific parachor = $\Phi = v\sigma^{1/4}$, where σ = surface tension and $\Phi = 1.838 - 0.00162p_S + 93 \times 10^{-6}\,t$.

(*D*) *Viscosity:* For 60 to 80% of SiO_2, log η = $0.0167\ p_S - 3.548 + (2658 + 43.55\ p_S)/t$, where η = viscosity.

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Molten Glass by Modified Dipping-Cylinder Method," *Jour. Amer. Ceram. Soc.*, **23** [1] 12–17 (1940).

(*b*) A. E. J. Vickers, "Effect of Atmosphere on Viscosity and Surface Tension of a Simple Glass," *Jour. Soc. Chem. Ind.* [London], **57** [1] 14–22 (1938); *Ceram. Abs.*, **17** [9] 302 (1938).

(*c*) C. A. Bradley, Jr., "Measurement of Surface Tension of Viscous Liquids," *Jour. Amer. Ceram. Soc.*, **21** [10] 339–44 (1938).

(*d*) Gustav Keppeler and A. Albracht, "Surface Tension of Glass, I–III," *Glastech. Ber.*, **18** [8] 201–10; [9] 236–45; [10] 275–80 (1940); *Ceram. Abs.*, **20** [3] 66; [10] 236 (1941).

See also footnotes 6 and 7.

[23] H. R. Lillie, "High-Temperature Viscosities of Soda-Silica Glasses," *Jour. Amer. Ceram. Soc.*, **22** [11] 367–74 (1939).

* The best straight-line relationship was obtained using $1/(t + c)$ instead of $1/t$, where c is a very small positive or negative constant; $1/t$, however, is more convenient for practical purposes.

QUALITATIVE SPOT TESTS FOR COMMON CONSTITUENTS IN GLASS*

By S. Zerfoss† and R. L. Hess‡

Abstract

A procedure is outlined for routine qualitative analysis of certain common constituents of glass by means of spot tests using organic reagents according to the technique of Feigl. Sampling of the glass has been accomplished previously by using the powdered glass or by attacking the glass surface. A technique is discussed for the nondestructive testing of fabricated samples. Using this technique, a sample may be obtained by scratching the glass against a quartz plate. The method shows promise as a practical laboratory and plant tool.

I. Introduction

During the past twenty years the chemist has perfected a special technique for the rapid identification of small amounts of material. This technique of microanalysis, while designed primarily for use in special laboratories, has found wide application in many technical fields. In the steel plant it is occasionally used by foremen to label various alloys with respect to their special metal content. The mineralogist has found the technique useful in the study of opaque minerals, and it is used in the inorganic chemical laboratories to study traces of impurities.

In its most highly developed form, microanalysis has been used for the complete quantitative and qualitative analysis of small samples (50 to 500 mg.). The qualitative analysis technique, however, can be rendered into a routine form for the use of nontechnical personnel on simple identification problems. It should be made clear that the use of the word "technique" does not imply something actually new by way of equipment or procedures but rather it implies a change in dimensions wherein the operator forces himself to deal with smaller equipment and samples.

It is the purpose of this paper to discuss the application of qualitative microanalysis to simple problems of identification and labeling of glass and raw materials in the glass plant or laboratory. It would be of interest occasionally to the plant operator to know the common or special chemical constituents of a particular sample of glass or cullet, for example, whether the glass contains potash or barium. The question can be simply and economically answered by the use of the microtechnique. This technique can be reduced in complexity to the point that single tests which are specific for an element require no special knowledge or skill on the part of the operator.

In the research laboratory, the chemist or spectrographer can provide an accurate qualitative analysis of any glass sample. In the steel plant, a complete quantitative analysis of a metal can be made within 30 minutes. While the precision of the microtechnique cannot compare with that of the chemist or the spectrographer, in those instances when a high precision is not required the speed and economy with which a microtest can be made make it a ready routine substitute.

Qualitative microanalysis refers to a method for dealing with amounts of material of the order of 10^{-6} gm. or as the microtechnician would put it, 1 gamma (1 gamma equals 10^{-6} gm.). This amount of material is commonly tested within concentration ranges of 1:100,000. The methods of analysis are based either (1) on the formation of a colored or fluorescent precipitate, complex, or solution or (2) the precipitation of a characteristic crystal or crystal aggregate, which can be identified by the usual crystallographic or petrographic technique. The first method is based on a reaction yielding a colored product just as in the case of ordinary qualitative analysis. The reaction is carried out within a volume of solution of less than 1 cc. on a filter paper or spot plate and is therefore called a "spot test".

The ideal reagent for an identification based on color is one which will selectively react with a specific ion in a mixture to give a characteristic color for that ion and reagent. Unfortunately no reagent possesses this property since most reagents yield precipitates with several ions and thus prevent an exact identification. The problem is solved by separating the complex solutions into the separate ion solutions and applying the reagent. A set of reagents has been worked out which will test specifically for an ion, provided separations have been made.

The choice of reagents has widened with the introduction of organic chemicals into analysis. In 1906, Tschugaeff was the first to introduce a complex organic chemical into analytical practice in the use of dimethylglyoxime as a test for nickel.

Since that first application, the analytical literature has been filled with reports of colored compounds of metal-organic composition. In rare instances, reactions have been found that were essentially specific; that is, the reaction of the organic compound with a particular ion takes place to form a compound of characteristic and unique color for that reagent. The dimethylglyoxime reaction for Ni^{++} is specific except for certain rare ions; by adjusting conditions of tests so that these rare ions are removed from solution, the test can be made specific.

In the case of nickel, the compound formed with the reagent has a definite composition and is well crystallized. This is not universal and many of the organic

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reactions yield absorption complexes of unknown composition which, however, are reasonably characteristic and reproducible. An example is the well-known pink alizarin lake formed when aluminum ion is precipitated in the presence of the alizarin solution.

II. Microtechnique

The microtechnique worked out for use on simple identification problems on glasses and their raw materials can be divided into four operations, (1) sampling and solution, (2) separation, (3) application of the reagent, and (4) evaluation of the test.

(1) Sampling and Solution

Most of the reactions mentioned herein will detect under ideal conditions the presence of 1 to 10 gammas within a concentration limit of 1 : 100,000. For the work in glass, the sample size required has been found to be from 1 to 10 mg. for elements present to the extent of 0.1 to 1%. A larger sample naturally can be used more effectively.

Since the ions in the glass are rendered insoluble to ordinary acids because of their inclusion in the silica network, the glass must be dissolved and the silica volatilized with HF. Under certain conditions, strong mineral acids will remove enough ion to permit the test, but the most satisfactory solution is obtained with HF treatment. Unfortunately, the HF in the resulting solution seriously interferes, in a negative manner, with the reactions of the organic reagents. It is therefore necessary to volatilize the residual HF and decompose any insoluble fluorides formed by addition of the H_2SO_4 to the solution.

The finely powdered glass sample is mixed in a platinum vessel with 10% HF solution (containing 10% of H_2SO_4) and slowly evaporated to dryness. The solution is repeated several times and finally the residue is taken up in 5 *N* sulfuric acid.

An alternative method of solution is the Na_2CO_3 or borax bead, but this procedure requires additional manipulation of the solutions not required in the more direct HF procedure. Niessner and Korkisch[1] use the HF method of solution effectively; they apply the solution reagents directly to the surface of the piece of glass to be tested.

Under certain conditions, it would be desirable to test the glass sample without destroying it or damaging the principal surfaces by an etch. A suitable nondestructive procedure has been worked out in this laboratory. A sample for analysis is taken by scratching the edge of the specimen against a roughened or sanded flat plate of rock crystal or silica glass. A photograph of the quartz plate is shown in Fig. 1. The resulting sample will represent from 0.1 to 0.4 mg. of material, depending on the conditions of the scratch. This scratch can be repeated several times until an adequate sample is obtained.

The sample, while still on the quartz plate, is taken into solution by transferring a 30% HF solution to it by means of a platinum loop. A loop (3 mm. in diameter) will deliver about 1.5 mg. of solution. Usually, for an ordinary soda-lime glass, 5 loopfuls of acid are adequate. The solution is speeded by stirring the powder with the Pt wire. Two loopfuls of 5 *N* H_2SO_4 are added and the solution is slowly evaporated on a hot plate. The solution can be repeated, the final extraction is made with H_2SO_4 alone, and the solution is transferred to the spot plate for tests.

FIG. 1.—Scratch plate for nondestructive sampling of glass.

It is necessary to have the H_2SO_4 present to prevent the volatilization of certain metals as fluorides, to dissolve the insoluble fluorides and convert them to sulfates, and to volatilize the residual HF.

(2) Separations

In standard qualitative analysis, a separation of the ions into groups must be made before specific tests for the ions are applied. For example, a solution of Zn^{++} and Al^{+++} ions is first treated with NH_4OH, thereby precipitating the Al^{+++} ions and effecting a separation of the ions for the specific tests.

Similarly, only in special cases can the organic reagents be applied to a mixed ion solution. For example, the dithizone reagent will react with fifteen elements to give colored complexes. These complexes may have different colors for each ion, but formed together in the same solution the colors interfere and prevent identification. In working out a test, it is therefore necessary to know the interferences and to include in the procedure such separations as will make the final test on the separated solution specific.

Interferences can be both positive and negative in character. In the case of positive interferences, the interfering ion will give a similar or identical reaction with the reagent. Negative interference involves the hindering action that some ions or radicals have on the ion to be tested for or on the reagent. For example, HF combines with many of the organic reagents by simple addition to a double bond and changes the behavior of the reagent.

Thus, in order to make a test procedure specific for an ion, the procedure must include such steps that will eliminate the positive and negative interferences.

Numerous schemes for the separation of the ions for microtests are available in the literature. For the relatively simple glass system, however, when the probable composition is fairly well known, separations are

[1] M. Niessner and F. Korkisch, "Microanalytical Test Procedures for Investigation of Glass," *Glastech. Ber.*, **19** [2] 33–39 (1941); résumé in *Glass Ind.*, **24** [12] 518–19 (1943) and **25** [1] 21–22 (1944); abstracted in *Ceram. Abs.*, **20** [10] 235 (1941).

not usually required. If a separation is required, the scheme of Smith and West,[2] involving the use of Na_2O_2–Na_2CO_3 to divide the solution, is probably the best procedure.

(3) Application of Reagent

The reagent is usually added as a solution in water or an organic solvent. It may, in special cases, be added as powder or a reagent paper can be prepared by soaking special filter paper in the reagent solution and drying the paper.

The tests can be carried out in spot plates, either black, white, or transparent, or on filter paper as the test may demand. Special filter paper called "confined spot-test paper" can be used to estimate the amount of a particular element. The confined spot-test paper[3] is a filter paper stamped with a ring of paraffin so as to outline a definite area of paper. Reactions carried out on these papers under identical conditions of reagent and test-solution concentration can be used to estimate amounts of material present.

(4) Evaluation of Test

The result of the test may be a colored solution, precipitate, or stain that is characteristic of the reagent and ion and differs from the color of the original reagent. It has been found advisable in all cases to check the color obtained against a known standard. For this purpose, a series of simple glasses has been prepared containing a third element present in amounts up to 2%. With these glass samples and others, the various tests recommended have been worked out and then tried on unknown samples. It was found that the HF interfered in all cases but that the other elements, Ca, Na, K, and Al, commonly present in glass, do not give serious interference.

It is often wise to run a blank test with the reagents in order to determine the color of such a solution. This precaution is made necessary by the fact that some of the reagents are unstable solutions which will react in time but which are catalyzed by the ion in the test solution.

III. Recommended Tests for Various Common Glass Constituents

A complete set of reactions for all of the elements is available in a book by Feigl.[4] This work is a collection of several organic or inorganic microreactions for each element from which the reaction best suited to the particular problem may be selected. The book contains an excellent discussion of the theory, the various reactions, and their application to spot tests. In a paper discussing interferences, Smith and West[2] have listed a series of specific tests and have included all necessary separations.

[2] L. Smith and P. W. West, "Interferences Occurring with Selected Drop Reactions," *Ind. Eng. Chem., Anal. Ed.*, **13**, 271–75 (1941).

[3] H. Yagoda, "Application of Confined Spot Tests in Analytical Chemistry," *ibid.*, **9**, 79 (1937).

[4] Fritz Feigl, Qualitative Analysis by Spot Tests. Nordemann Publishing Co., Amsterdam, 1937.

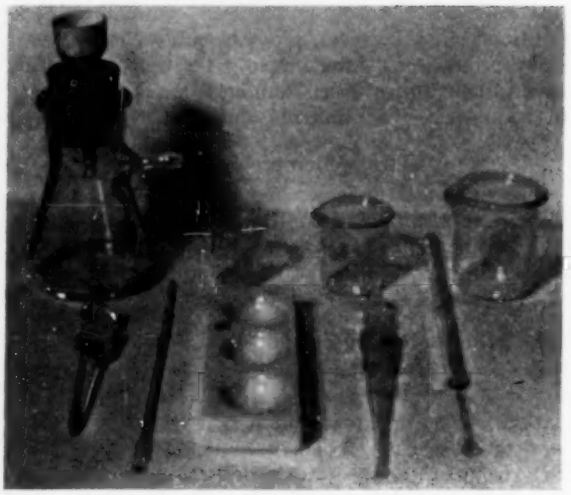

FIG. 2.—Apparatus for spot tests (1/2 ×).

Niessner and Korkisch[1] have presented procedures for tests of the colored constituents of glass. Feigl[4] has suggested simple tests for some of the other constituents. It is the purpose of the autnors to indicate simple tests for the common uncolored constituents. These procedures are quite simplified and do not apply to the analysis of other more general solutions.

The following apparatus shown in Fig. 2 is required for these tests: (1) white spot plate (3 or 12 cavities), (2) black spot plate (3 cavities), (3) small pipette or rod delivering approximately 0.05 to 0.10 drop, (4) quartz plate (see section II (1) and Fig. 2) 2 by 2 cm., (5) Pt wire in holder, (6) 5, 10, and 25 cc. beakers, (7) Büchner-type microfilter with flask, and (8) stainless steel spatula.

The organic reagents for these tests were purchased from Eastman Kodak Company. Filter paper for the tests and for the preparation of reagent papers should be fine-grained quantitative paper similar to type of Schleicher and Schüll No. 589. This paper can be used for the preparation of the "confined spot-test" papers previously mentioned.

All test solutions are prepared in the manner described in section II (1); either a sample scratched on the quartz plate or from powdered glass may be used. It is essential that the test solution be as nearly neutral as possible before the addition of reagents. When small drops are added to a small volume, a drop of fairly strong acid will make a large change in the pH and possibly render the test invalid. Too much acid-base addition will concentrate the solution in neutral salts.

For these tests, the Feigl book[4] and the work of Smith and West[2] have been drawn on freely. Modifications of the procedures worked out in this laboratory have been included.

(*A*) *Detection of Calcium:* No simple test for calcium is available. It is necessary to separate calcium from the ions of the first three analytical groups (Pb^{++}, Cu^{++}, Zn^{++}, Al^{+++}, etc.) by means of $(NH_4)_2S$. The filtrate from this separation, containing only the 4th and 5th group elements, is used as the test solution.

The reagent, dihydroxy tartaric osazone,* is added to the test solution either as a fine powder or as a freshly saturated water solution. The test is best carried out on a black spot plate. If Ca^{++} is present, a yellow precipitate will form in the solution. Unfortunately, Be^{++}, Ba^{++}, and Sr^{++} form similar precipitates and their presence must be tested for separately.

(*B*) *Detection of Lead:* The test for lead is made with the carminic acid† reagent. A test paper is prepared by soaking filter paper in the reagent solution (a 0.5% solution of carminic acid in 10% NH_4OH) and allowing the paper to dry. The test solution is treated with several drops of a solution of NH_4OH and NH_4Ac to eliminate any interferences and filtered. A drop of the solution is placed on the test paper and the paper is allowed to dry. The appearance of a violet spot indicates the presence of lead. This test is essentially specific.

Dithizone is also recommended as a reagent‡ but a separation with KCN is required to eliminate interferences.

(*C*) *Detection of Barium:* The test for barium is carried out on filter paper; the reagent, sodium rhodizonate,§ is used in the form of a freshly prepared 5% water solution. As in the case of Ca^{++}, a $(NH_4)_2S$ separation is required. The filtrate from this separation is acidified and the reagent is added. If Ba^{++} is present, a red-brown stain will develop on standing; this stain will fade slowly when HCl is added. There is no interference except for Sr^{++} whose stain fades rapidly with the HCl addition.

(*D*) *Test for Phosphorus* ($PO_4^{\equiv}$): The standard reaction with $(NH_4)_2MoO_4$ is the basis for the phosphate test.[2] The test solution, acidified with HCl, is evaporated to dryness and extracted with HNO_3 thus eliminating any interference from Si^{++++} and As^{+++}. The test is carried out on a spot plate. Two drops of the $(NH_4)_2MoO_4$ solution are added to the test solution followed by an addition of a drop of HNO_3 and $SnCl_2$. A blue color develops if $PO_4^{\equiv}$ is present. There are no interferences. Benzidine‖ can also be used as a reagent.

(*E*) *Test for Boron:* A number of reagents have been suggested for the boron test, but the flame test¶ seems to be the simplest and most practical test. This test can be made during the solution of the glass on the quartz plate. The fumes of BF_3 coming off the evaporating solution impart a green color to the flame. The Merwin screen can be used to intensify the effect.

Neelakantam and Row[5] have worked out a fluorescent test for boron. A solution of borate is acidified with acid and a drop of resacetophenone and several drops of syrupy H_3PO_4 are added. A blue fluorescence appears under ultraviolet light.

The test solution is acidified with acetic acid on a spot plate and several drops of syrupy H_3PO_4 are added. A drop of the reagent, a saturated alcoholic solution of resacetophenone, is added and the drop is examined under a long-wave ultraviolet lamp. A brilliant blue fluorescence indicates $BO_3^{\equiv}$. The reagent solution shows a weak orange fluorescence. The test is specific for the common constituents found in glass.

(*F*) *Detection of Titanium:* The standard test for titanium with H_2O_2** as a reagent is used for the microreaction. The reagent is a 10% solution of H_2O_2. To the test solution in a spot plate is added a drop of H_3PO_4 and a drop of reagent. A yellow color indicates the presence of titanium. Vanadium, chromium, and molybdenum give positive interference and require a Na_2O_2-Na_2CO_3 separation to make the test specific. Since their presence is not common in glass, this separation is not usually required.

(*G*) *Detection of Aluminum:* The aluminum test with alizarin†† requires a separation with NaOH. The test solution is treated with NaOH and filtered. The filtrate, containing the Al^{+++}, is acidified with HAc. The test for aluminum is made by placing a drop of the test solution on a piece of alizarin paper (prepared by soaking filter paper in a saturated alcohol solution of alizarin and drying) or adding a drop of the alizarin solution to the test solution. When the moistened test paper is made ammoniacal by holding over NH_4OH, a violet color indicates the presence of Al^{+++}.

A test can also be made with morin (saturated alcohol solution of morin). To the test solution, acidified with HAc, is added a drop of the reagent. Under the ultraviolet lamp, a green fluorescence indicates the presence of Al^{+++}. These tests are specific for ordinary glass providing the separation has been made.

(*H*) *Detection of Zinc:* The test for zinc‡‡ can be carried out on the quartz solution plate and does not require the complete removal of the HF solvent. The reagent consists of two solutions which are freshly mixed before the test. Solution (1) is a 2% water solution of $K_3Fe(CN)_6$; solution (2) has 0.5 gm. of diethylaniline in 200 cc. of syrupy H_3PO_4. The two solutions are mixed in the proportions of 3 to 2, respectively. The addition of a drop of the mixed reagent to the test solution yields a brown color if Zn^{++} is present. Occasionally the color is slow to develop but it should form within three minutes. A blank test should be run. The test is specific for the glass constituents.

(*I*) *Detection of Magnesium:* Magnesium is tested for with titan yellow§§ (0.1% water solution). To the test solution in a spot plate is added a drop of KCN solution, a drop of reagent, and a drop of 5*N* NaOH. A red-to-orange color indicates the presence of Mg^{++}. The test is specific for glass, and the KCN can be omitted if Zn^{++} is known to be absent.

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* See Smith and West, footnote 2; also Feigl, footnote 4, p. 134.

† See Feigl, footnote 4, p. 32.

‡ See Smith and West, footnote 2; also Feigl, footnote 4, p. 33.

§ See Smith and West, footnote 2; also Feigl, footnote 4, p. 131.

‖ See Feigl, footnote 4, p. 205.

¶ *Ibid.*, p. 330.

[5] K. Neelakantam and L. R. Row, "New Fluorescence Reaction for Detection of Boric Acid," *Proc. Indian Acad. Sci.*, **16A** [Nov.] 349–58 (1942); *Ceram. Abs.*, **22** [10] 183 (1943).

** See Smith and West, footnote 2; Feigl, footnote 4, p. 120.

†† See Feigl, footnote 4, p. 114.

‡‡ *Ibid.*, p. 107.

§§ *Ibid.*, p. 137.

(*J*) *Detection of Potassium:* Potassium can be detected in the presence of the normal glass constituents by the use of sodium cobaltinitrite[5] ($Na_3Co(NO_2)_6$. The test solution, on a black spot plate, is treated with a few drops of HAc and a few grains (or a saturated solution) of the reagent. A yellow precipitate indicates the presence of K^+. Lead gives a similar precipitate, which is soluble if the solution is warmed.

Gabriel and Cox[6] have used this test to differentiate quartz and feldspar grains in a mixture. The mixed grains are exposed to HF fumes and then treated with the reagent solution. The quartz remains clear, plagioclase feldspar is clouded, and microcline or orthoclase (containing K^+) is colored yellow.

(*K*) *Limits of Detection:* The smallest amount of an ion that can be detected by means of the microreactions is of the order of 10 gamma or less, depending on the conditions of the solution and the number of interferences. For simple inorganic solutions, the limit is much smaller than for solutions derived by HF treatment of a glass. No attempt has been made to estimate the limits of identification for the recommended reactions because the writers were interested in providing simple tests for reasonable (rather than minute) quantities of material.

For example, a series of synthetic samples containing 0.01, 0.1, 1.0, and 3.0% of K^+ and Al^{+++} were tested by the recommended tests. A satisfactory test for either ion could be obtained for the 0.1% mixture. Such a survey would indicate the practical limits of identification for these ions.

IV. Conclusions

(1) Procedures for testing the common constituents in glass by means of the spot-test technique have been presented in a form suitable for routine work in the plant; (2) a technique for the nondestructive sampling of glass samples has been worked out; and (3) details are given for solution of the sample in HF.

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[5] *Ibid.*, p. 144.

[6] A. Gabriel and E. P. Cox, "Staining Method for Quantitative Determination of Certain Rock Minerals," *Amer. Mineralogist*, **14** [8] 290–92 (1929); *Ceram. Abs.*, **8** [11] 847 (1929).

TECHNOLOGICAL DEVELOPMENT OF POTTERY IN NORTHERN SYRIA DURING THE CHALCOLITHIC AGE*

By Frederick R. Matson

Abstract

The techniques of manufacture and decoration employed by the potters living on the Plain of Antioch from about 4500 to 2000 B.C. are summarized on the basis of evidence obtained from a laboratory study of the pottery and the local clays.

I. Introduction

Pottery and chipped flints are the oldest remains of communal life in the ancient Near East. When nomads started to settle down in one spot for several months at a time in order to have a more certain supply of food from crops and the domestication of animals, they built mud houses and made pottery. The earliest ceramic products must have been very crude and were probably sun dried. These have long since disintegrated. Some of the oldest pottery so far found is that which was excavated in the Plain of Antioch by the Syrian Expedition of the Oriental Institute of the University of Chicago. Large quantities of sherds (broken pieces of pottery) from each occupational level uncovered were brought back to Chicago for study after preliminary sorting in the field. They form a continuous ceramic sequence from about 4500 to 2000 B.C.†

Indestructible ceramic fragments such as these are almost the only remaining clues to an understanding of how people lived in the Near East in those early times, for practically all other evidence has decomposed. A detailed analysis of the shape and decoration of the pottery and a comparison and evaluation of it with related materials from its own and other sites is being prepared by Braidwood.[1] His work is of fundamental importance in the field of Near Eastern archeology.

This large collection of carefully catalogued potsherds is almost unique among excavated materials since most archeologists are able to bring home only complete or restorable vessels and a small sampling of sherds. It presented an excellent opportunity to study the very early development of ceramic techniques in an isolated area where the variety of raw materials available was limited. Dr. Braidwood kindly made the sherds available for such work.[2]

II. Area and Materials Studied

The Plain of Antioch, known to the natives as the

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Design Division). Received October 3, 1944.

† Dates in this early period are only rough approximations. The cultural sequences were labeled "Phases" by the excavators. The Chalcolithic period (the Copper Age when metals were first used) comprises Phases A (the earliest) through J.

[1] This work will be published by Robert J. and Linda S. Braidwood, "Excavations in the Plain of Antioch, I," *Univ. of Chicago, Oriental Inst. Publ.*, LXI.

[2] A discussion of the technological approach to the study of ancient pottery can be found in a paper by F. R. Matson, "Research Problems in an Archeological Ceramic Laboratory," *Bull. Amer. Ceram. Soc.*, **20** [12] 451–53 (1941).

FIG. 1.—The Plain of Antioch.

Amuq, is a mountain-girt area a few miles east of Antioch in what was northwestern Syria until annexed by Turkey in 1939 (Fig. 1).* Clays are deposited in the Amuq by three rivers (one of which is the Orontes) and several mountain streams. On the mountains can be found outcrops of limestone, sandstone, slate, and basalt.

Small clay samples from four points in the plain were obtained for study. Their mineralogical impurities were identified by means of sieve analyses, heavy mineral separations, and thin sections. Color development and firing characteristics at temperatures up to 1100°C. were determined in an electric furnace. The amounts of clay were not large enough for the measurement of many physical properties.

The local potters had available two general types of clay that were at times blended in the plain deposits. (1) A sandy red-firing clay from the mountain slopes and their outwash which had a very short working range. It was a good slip clay when levigated, and dried surfaces of it took an excellent polish. (2) A buff- to salmon-firing clay from the plain that had good working properties. It contained a variable amount of calcite and many minerals derived from weathered basalts. Dried surfaces dusted instead of receiving a polish. When salted tempering water was used, the fired color of the clay at the higher temperatures was yellow.

FIG. 2.—Excavations at Tell Judaidah.

Most of the colors appearing on the Amuq sherds could be duplicated with these clays. A knowledge of the mineralogical impurities in them was most useful in interpreting the thin sections of the pottery.

After 3000 sherds from all of the periods being studied

* Figure 1 was taken from the lower mountain slopes on which were limestone outcrops and red clay. To the right can be seen the expedition house and the modern village of Rihaniyah. Tell Judaidah from which much of the pottery was obtained can be seen in the foreground. In the distance are other mounds.

Figure 2 shows Tell Judaidah with the step trench exposing the successive cultural levels. The Chalcolithic layers are in the lower third of the mound. On top of it were the ruins of an early Christian church.

were examined under a binocular microscope for textural differences, 308 were selected as representative for thin sectioning. The sections, which were prepared with the aid of workers on a WPA project, were classified according to their mineralogical fabric. These data together with those from the raw clays, the examination of sherds for the indications they gave of workmanship, and refiring tests of the sherds supplied the information for the outline of ceramic evolution in the Amuq during the Chalcolithic Age.*

III. Development of Pottery Techniques

The oldest pottery was found below the present-day ground-water level. It was of two types. The first comprised simple vessels with walls 10 to 20 mm. thick made of straw-tempered calcareous clay from the plain. The vessels were fired sufficiently to oxidize the surface areas but usually the core was black due to the presence of unoxidized carbonaceous materials. A dull red slip was occasionally applied to the exterior surfaces of the pots. The walls were uniform in thickness and the surfaces were smoothly finished.

The second type was a thinner (5 to 10 mm.) better-made ware with a carefully burnished exterior surface (Fig. 3). At one village site, the mountain clay that can take a good polish was used; at another, the plain clay was employed with a surface slip of the mountain clay. The potters at this early time recognized the difference in the finishing properties of clays and knew the value of slips.

The burnished ware received an intentional surface blackening. Many sherds when examined along a broken edge can be seen to have a black layer 1 mm. thick at the surface; below this is an oxidized zone, under which is a black core. During the firing, the temperature was high enough to oxidize the surfaces but not the core. It was probably about 600°C. In the last stages of the firing, green wood or cow dung was used to produce a smoky reducing atmosphere, after which the kiln was sealed and allowed to cool. This is an interesting technique that continued in use in the Mediterranean area for 3000 years.[8] The Trojans, Greeks, and Etruscans used it to obtain their black-surfaced pottery. The fine ware of the American Indians at Moundsville, Alabama, also has a black surface above an oxidized layer.

It is evident that the potters of the Amuq had some knowledge of the color properties of a kiln atmosphere. The utility ware had oxidized surfaces often marred with black blotches, while the burnished vessels were usually black in color. The few pieces that were red or brown may have come from places in the crude kilns where there was a leak and fresh air could enter during the cooling-down period. The burnished ware was made for a long time. Pattern burnishing and incised designs were sometimes used. Late in this period, the desire for a dark surface tended to die out and the pottery was more often red.

FIG. 3.—Pattern burnished jar.

When the burnished vessels were still being made, painted pottery began to appear in Phases B and C. The earliest pieces, to judge from their thin sections, were mostly imported. They probably came from several different places as their pastes are quite variable in composition. Soon a local decorated product occurred in large quantities. It was made by hand from very fine-textured plain clay. The clay either came from water-washed deposits or was levigated by the potters. Four fifths of the sherds were oxidized throughout and the remainder had oxidized surfaces. This is the earliest uniformly well-fired ware. The colors, when compared with the test pieces of the local clays, indicate that the firing temperature was about 800°C. A ferruginous paint (probably derived from the red mountain clay) applied with a brush was used for the decorative motifs. The paint is red when the sherd surfaces are buff to cinnamon in color (80%) and black when the clay is yellow (20%). This would indicate that the kilns were fired under predominantly oxidizing conditions but that in some sections or during some firings reducing conditions existed. It is possible that a new type of kiln or a better way of firing the old ones was introduced by the traders or immigrants who brought with them the painted pottery style.

Imported pottery of a design type known as Halaf greatly influenced it, even if it did not give rise to the local decorated ware of Phase C. The Halaf pottery came from the east. It was extremely fine textured and had a vitrified black paint on a yellow clay ground. The imported Halaf sherds found in the Amuq are identical in appearance and thin section with pieces from northern Iraq and northeastern Syria.

The next major development represents an eastern influence which arrived in considerable force late in

* A detailed report on the various phases of this study will appear as a chapter in Dr. Braidwood's forthcoming volume.

[8] The oxidation of black sherds and their subsequent reduction in the laboratory to their original color is described by V. Gordon Childe, "On the Causes of Grey and Black Coloration in Prehistoric Pottery," *Man*, **37** 43–44 (1937). He found that the reduction of the iron in the clay was the cause of the black coloration. The deposition of carbon was of very secondary importance as a colorant.

FIG. 4.—Vessel of the Obeid period.

Phase D. The Obeid pottery as it is termed shows distinct ceramic progress (Fig. 4). It is the first high-fired ware to appear. Almost one fifth of the Obeid sherds are yellow-green in color (1050°C.), two fifths are yellow (900° to 1000°), and the remainder are buff (800° to 900°). Many of the yellow-green sherds are warped; they must have come from hot spots in the kiln. Doubtless all three colors were produced in each firing. By now (still well before 3500 B.C.), the potters knew how to design and control their kilns so that they could obtain as high temperatures as the clay would stand. (The plain clay is almost completely vitrified at 1100°, the mountain clay at a lower temperature.) To judge from the very fragmentary remains of kilns of later periods, those used were most likely of a simple updraft type and were shaped like beehives.

The Obeid pottery is decorated with a semivitrified iron paint which is dark brown on the buff and black on the yellow sherds. It occasionally shows blisters. This ware was made throughout many parts of the Near East. It is the earliest type of pottery so far found in lower Mesopotamia, an area long considered the birthplace of civilization; yet, farther north, pottery had been made for several hundred years before the Obeid style appeared.

In the centuries before 3500 B.C., copper was used but it was a rare and expensive item. The large utility vessels were still made of clay tempered with chaff and were low fired. A close examination of sherds of the finer ware of this period indicates that a major ceramic development occurred—the Amuq potters had begun to make some of their vessels on a wheel. Well-levigated clay was used, and the rims were carefuly finished. This is the first group of sherds in which it is quite certain that the clay was levigated. Few mineral grains were seen in the thin sections that were larger than 0.02 mm. A characteristic wheelmade shape was a

FIG. 5.—Very early wheel-made bowl.

FIG. 6.—"Reserved slip" decoration.

very fine-textured, straight-sided bowl about 10 cm. in diameter (Fig. 5). It had a slightly everted rim and a somewhat convex base. The walls were 4 to 7 mm. in thickness. This form is clearly one which is best suited for manufacture on a wheel. The vessels were very high fired for they are yellow-green in color. No decoration is used in Phase F except occasionally a red slip on a few large vessels. Apparently with the advent of the wheel, painted designs temporarily disappeared.

At the beginning of the third millennium B.C., there was more variety in the kinds of plants and animals that were domesticated. The technique of casting copper was developed and there was a decline in the use of flint and bone tools. Cylinder seals of a southern Mesopotamian type were found in the Amuq. This indicates widespread trade relationships which had earlier been suggested by some pottery designs and by imported sherds. The potters produced a well-fired, wheelmade ware with slip applied by a brush in simple bands on the exterior surfaces. Archeologists have inappropriately termed this a "reserved slip" decoration

FIG. 7.—Multiple brush design.

(Fig. 6). Pleasing effects were obtained with very simple linear designs.

Later, in Phase G, paint was again used, this time in a "multiple-brush" technique (Fig. 7). Three or more brushes were held in a row in the decorator's hand and were used to apply a multiple wavy band design to fine-textured small bowls and jars and occasionally to larger and coarser vessels.[4]

When the first dynasty of Egypt was flourishing, the Amuq was producing two distinctive types of pottery. The first, termed "brittle-orange," was made of a red-firing clay containing small grains of slate and quartzite. The impurities in the clay are unlike those found in any other of the pottery types studied. Sherds of this ware occurred in fair quantity in several of the mounds that were the remains of ancient village sites, so it is likely that the "brittle-orange" pottery was made at a village at some place in the Amuq plain where the red mountain clay was associated with slate and quartzite outcrops. The pottery is of varying shades of red with a smoothly finished, dull undecorated surface. It was fired between 900° and 1000°C. to judge from sherd refiring experiments. When burnished sherds of the earliest pottery found in the Amuq were refired to 1000°, they were indistinguishable in appearance from the "brittle-orange." This is the first use of the red clay since the technique of painted designs arrived in the Amuq.

The second type of pottery, the "red-black," was made in Turkey, Syria, and Palestine. Its distinctive features are its glossy red and black surfaces on which the polishing marks cannot be seen and the surface fluting that occurs on the larger vessels (Fig. 8). The clay is quite calcareous so there is an upper limit of 800° to 900° to the firing temperature. Sherds that were refired to 1000° disintegrated within a few months as the lime hydrated. The red surface coloration is almost always produced by a slip of the mountain clay. Some of the vessels were also made of this clay but most of them were of the plain clay. Almost half of the sherds had a red exterior which was accompanied by a red or tan interior surface. Most of the remainder had black exteriors. Tan is the natural fired color of the clay. Black occurs only on the exterior surface and penetrates into the sherd from 1 to 8 mm. The interior surface is almost always red or tan and the rim is frequently red. When black sherds are refired, they become tan. The black coloration could not have been produced by a reducing atmosphere in the kiln because then the interior surfaces would also have been darkened. This is not the case. Apparently an organic material, such as oil, grease, or resin, was rubbed on the outer surfaces right after the vessels were removed from the kiln while they were still hot enough to carbonize the applied substance as it penetrated into the walls or the vessels were dipped almost up to the rim in an organic liquid. The thickness of the black-colored layer varies, but it is uniform in an individual sherd. This technique of black surfacing can be much better controlled to limited areas and is far more flexible than the one used by the earliest Amuq potters in their burnished ware. It is one of the most attractive and colorful styles that the potters developed.

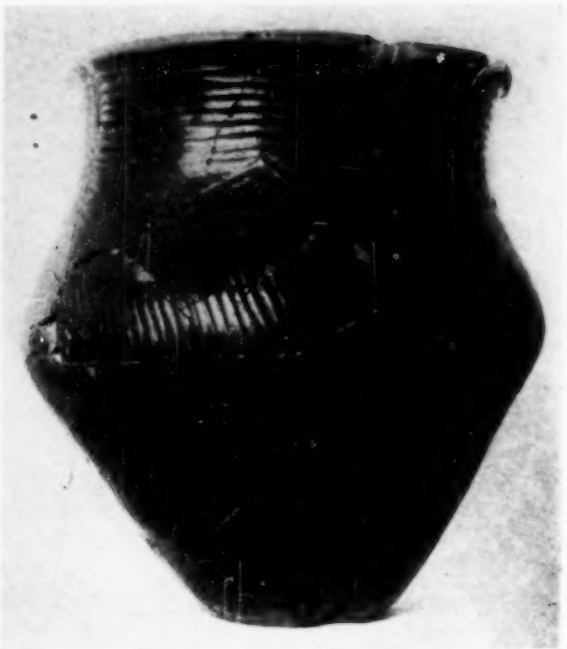


FIG. 8.—"Red-black" polished jar.

The "red-black" ware is the last distinctive technological ceramic development in the pottery sequence being studied. As time went on, the potters learned to adjust the texture of the clay for the size of the vessels being made. Delicate goblets with walls only 3 mm. in thickness were produced in Phases I and J. They were often decorated with a band of iron paint, which, when dry, was incised so that pleasing designs resulted. An over-all wash with a thin paint was used on some of the pottery.

IV. Summary

As the beginning of the second millennium B.C. approached, writing was being evolved and written docu-

[4] R. J. Braidwood, "Note on a Multiple-Brush Device Used by Near Eastern Potters of the Fourth Millennium B.C.," *Man*, **39** [187] 192–94 (1939).

ments began to appear. Stone molds were made for the casting of metal tools. Many crafts were still in their early stages of development but the potters already had a long history of achievement. They had learned how to control the temperatures in their kilns reasonably well and were aware of the suitability of certain clays for the various decorative techniques. Higher kiln temperatures were gradually achieved, clay was levigated, the potters' wheel was introduced, and ware of good quality with a plain surface or with a slipped, painted, burnished, incised, or fluted decoration was produced. Many if not most of these techniques certainly did not originate with the potters living in the Amuq, the Plain of Antioch, but the continuous ceramic record of successive centuries that has been uncovered there and preserved is unique. It furnishes the materials for an early chapter in the distinguished history of one of the oldest crafts.

Acknowledgment

The author wishes to express his appreciation to Robert J. Braidwood for supplying the pottery and patiently discussing its problems, and to Carl E. Guthe, Director of the University of Michigan Museums, for permission and facilities to undertake this cooperative project with the Oriental Institute. The photographs used in this paper have been supplied through the courtesy of the Oriental Institute of the University of Chicago.

NOTE: Since the presentation of this paper, the author has joined the Research Laboratories of the Armstrong Cork Co., Lancaster, Pa.

CLASSIFICATION OF NATURAL ORGANIC BINDERS*

BY EDWARD P. MCNAMARA AND JAY E. COMEFORO

ABSTRACT

Modulus of rupture, loss on tumbling, migration, water absorption, and burn-out characteristics were studied using a series of organic compounds representative of the types used as binders for ceramic materials. The results are interpreted in terms of the constitution of the organic compounds and in terms of the mechanism of specific adhesion. The binding strength of an organic material may be predicted from a knowledge of its molecular constitution.

I. Introduction

Most studies of organic binders for ceramic bodies have been made by adding the binder to a body of definite composition and water content and determining whether or not the binder gives satisfactory results under these conditions. Usually the material works well, poorly, or not at all as a binder under the conditions in which it is being used. The results of such tests make it very difficult to compare in an exact way the effects of different materials. In addition, no standard tests or procedures exist for the evaluation of binders to be used for ceramic purposes.

In this study, the term "binder" is defined as a material which will give strength to a dry body. This definition distinguishes binders from plasticizers, which are materials that give bodies plasticity and plastic strength when they are mixed with water.

This present study was undertaken in an effort to determine whether certain tests can be conducted, the results of which will make it possible to classify and compare the binding power of the various types of organic materials which are used for the purpose of obtaining dry strength.

II. Review of Literature

A review of the literature reveals very few papers dealing with binders for ceramic bodies.[1] The most helpful sources of information are studies carried out by men associated with the glue industries, such as Bogue,[2] Scherer,[3] and Alexander[4] and the biological and physical chemists, notably Lloyd,[5] Eynon and Lane,[6] Norman,[7] Lewis, Squires, and Broughton,[8] Adam,[9] McBain and Lee,[10] McBain and Hopkins,[11] Garard,[12] and Branch and Calvin.[13]

* Presented at the Autumn Meeting, White Wares and Materials and Equipment Divisions, Uniontown, Pa., September 16, 1944. Received October 9, 1944.

[1] (*a*) E. S. Foster, "Organic Agents as Aids to Adhesion and Suspension of Glazes," *Jour. Amer. Ceram. Soc.*, **12** [4] 264–69 (1929).
(*b*) A. I. Andrews, G. A. Bole, and J. R. Withrow, "Making Dolomite Brick and Study of Their Properties," *ibid.*, **8** [3] 171–90 (1925).

[2] R. H. Bogue, Chemistry and Technology of Gelatin and Glue, 1st ed. McGraw-Hill Book Co., Inc., New York, 1922.

[3] R. Scherer, Casein, 3d ed. Scott, Greenwood & Son, London, 1921.

[4] Jerome Alexander, Glue and Gelatin. Chemical Catalog Co., Inc., New York, 1923.

[5] D. J. Lloyd, Chemistry of Proteins. P. Blakiston's Son & Co., Philadelphia, Pa., 1926.

[6] L. Eynon and J. H. Lane, Starch, Its Chemistry, Technology, and Uses. W. Heffer & Sons, Ltd., Cambridge, 1928.

[7] A. G. Norman, Biochemistry of Cellulose, Polyuronides, Lignin, etc., pp. 119–50. Clarendon Press, Oxford, England, 1937.

[8] W. K. Lewis, Lewis Squires, and Geoffrey Broughton, Industrial Chemistry of Colloidal and Amorphous Materials. Macmillan Co., New York, 1942. 540 pp.

[9] N. K. Adam, "Structure of Surface Films on Water," *Jour. Phys. Chem.*, **29** [1] 87–101 (1925).

[10] J. W. McBain and W. B. Lee, "Nature of Adhesion," *Chem. Trade Jour.*, **91**, 188 (1932); *Ceram. Abs.*, **11** [12] 636 (1932).

[11] J. W. McBain and D. G. Hopkins, "Adhesives and Adhesive Action," *Jour. Phys. Chem.*, **29** [2] 188–204 (1925).

[12] I. D. Garard, Applied Chemistry. Macmillan Co., New York, 1924.

[13] G. E. K. Branch and Melvin Calvin, Theory of Organic Chemistry. Prentice-Hall, Inc., New York, 1941.

III. Procedure

(1) Materials

The materials chosen as binders for this investigation are given in Table I.

These materials were selected, not so much because they are used as commercial binders but because they represent the several types of natural organic materials having adhesive qualities.

The percentages of binder used were 2 and 5%. The high percentage was used in order to exaggerate the effect of the binder. The binders were incorporated in a pure potter's flint (200- to 325-mesh) body. Flint was used in place of a normal ceramic body in order to eliminate any effects which might arise owing to the nature of the material. Pulverized quartz has no cleavage or definite grain shape nor does it have any natural tendency to bind itself together.

(2) Body Preparation

The binders were mixed with the flint by one of two methods as follows: (1) The dry binder was added to the dry flint in a Simpson laboratory mixer and blended for 20 minutes, after which 15% of water was added and the batch wet mixed for an additional 20 minutes, or (2) the binder, prepared as a solution or emulsion, was added to the dry flint during a period of 20 minutes and blended for an additional 20 minutes. The batches were based on 5000 gm. of dry flint, and a total of 780 cc. of water was used in all samples.

The wet body was granulated through a 14-mesh screen, and the granules were allowed to air dry until the water content approximated 12%, 8%, 4%, and, in some cases, lower.

A series of at least seven bars was pressed from the body at each of the approximate water contents specified. The bars were pressed uniformly at a pressure of 3 tons per sq. in. on a laboratory hydraulic press. The bars were $4^1/_8$ by $1^1/_8$ by (approx.) 1 in. in size.

Immediately after pressing, each bar was weighed, numbered, and placed in a drier at 180°F. for approximately 18 hours. The dry bars were reweighed, and the percentage of water at pressing was calculated.

IV. Test Procedures and Results

(1) Modulus of Rupture

The modulus of rupture was calculated from the breaking loads determined by means of a transverse-strength breaking machine using a 3-in. span. Modulus of rupture results are given in Table II.

Figure 1 shows the values of modulus of rupture versus water content at pressing for gelatin, casein, and peptone; it also includes the values for gelatin when added as a dry powder. Only one valid result was obtained when 5% gelatin was added wet due primarily to laminations occurring in the samples. This single point is significant for it shows that, at a comparable water content, gelatin has the highest modulus of rupture.

With the same binder content, the results show decreasing strength in the order of gelatin, casein, and peptone. Peptone, however, shows somewhat different characteristics than do gelatin and casein; it exhibits higher values when pressed with low water content. All curves giving values of modulus of rupture versus water content at pressing appear to have a characteristic shape, that of a double *S*. The scarcity of data available at this time does not justify drawing the curves to this shape. At a certain high water content, each binder exhibits a maximum modulus of rupture. It is believed that this effect is due to the filling of all pores by the mucilaginous mass of binder and water. When the water content at pressing is higher than this point, water is extruded from the body during pressing.

TABLE I

MATERIALS FOR BINDERS

Material	Description
Gelatin	Unflavored commercial gelatin with ash content less than 2%; water content about 15%
Casein	Pure washed casein derived from milk (Eimer and Amend)
Peptone	Pure peptone derived from meat (Eimer and Amend)
Gum ghatti	Commercial gum; water content 12%, ash content 2 to 3%
Commercial dextrin	Low soluble white corn dextrin (Stein-Hall, Inc., RH No. 4)
Dextrin N. F.	Specifications according to those of National Formulary; about 90% dextrin, not over 10% moisture, 0.5% ash
Corn flour	Moisture 7%, ash 0.4%, fat or oil 0.8%, carbohydrate 83.5%, protein 8.3% (Illinois Cereal Mills, Inc., Cere-amic)
Wax emulsion	Paraffin wax emulsion, 47% wax (Socony-Vacuum Oil Co., Inc., Ceremul 'C")

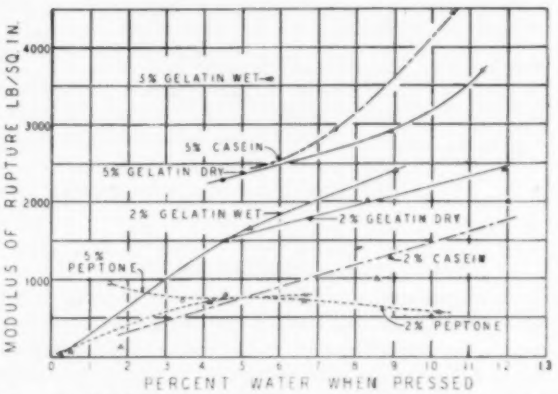


FIG. 1.—Modulus of rupture vs. water content when pressed for protein binders.

Figure 2 presents curves for another group of binders. The range of modulus of rupture values is greatly reduced, the highest value given being less than 1000 lb. per sq. in. Gum ghatti has modulus of rupture values intermediate between casein and dextrin N. F. It also shows high strength values at the lower water contents. The dextrin N. F. is stronger than the commercial dextrin. Corn flour falls in the same range as dextrin N. F.

The wax emulsion shows little change in modulus of rupture values with changing water content at pressing. It is believed that the wax prevents the water from wetting the quartz grains and that its effect is thereby neutralized. The dry wax itself is soft and allows the

TABLE II

SUMMARY OF RESULTS

Binder	% binder	Added as	Water when pressed (%)	Modulus of rupture (lb./in.²)	Tumbling loss (%)	Modulus of rupture / % tumbling = R	Water absorption (%)	Pressing range (% water)	Pressing characteristics
Gelatin	2	Dry powder	11.9	2405	9.42	256	0.81		Good
			8.25	2010	10.9	185		15–4	"
			4.63	1500	17.1	87.8	0.87		Poor
Gelatin	2	20% solution	9.02	2400	12.9	195			Good
			5.20	1670	19.7	84.8		15–1	"
			0.50	70	51.3	1.37			Fair
Gelatin	5	Dry powder	11.3	3680	3.46	1060	1.91		Good
			8.90	2910	3.70	787		15–4	"
			4.50	2290	4.95	463	1.85		Fair
Gelatin	5	32% solution	9.92	*					Poor
			5.75	3600 †	5.20	692		12–5	"
									"
Casein	2	13% solution	12.0	2010	15.9	126	0.65		Very good
			8.57	1015	21.8	46.7	0.66		" "
			4.57	805	30.8	26.1		15–1	Good
			1.85	135	‡				"
Casein	5	32% solution	10.5	4480	3.31	1350	1.50		Good
			7.44	2940	3.42	860	1.35	15–3	"
			5.45	2480	3.75	662			"
Peptone	2	40% solution	10.2	595	13.4	44.4	2.11		Fair
			6.66	720	10.4	69.2		11–1	Good
			4.20	715	21.2	33.7	2.19		"
			0.30	30	§				Poor
Peptone	5	50% solution	6.70	800			3.26		Fair
			3.45	725	4.75	153		9–1	Stick
			1.52	955	5.00	191			Fair
Gum ghatti	2	Dry powder	12.4	850	16.5	51.5			Laminated
			7.15	680	32.4	21.0	1.38	14–5	Fair
			6.48	720	31.4	22.9			"
Gum ghatti	5	Dry powder	12.2	3500‖					Laminated
			9.17				2.40	9–2	"
			1.15	605	22.9	26.6			Satisfactory
Dextrin N. F.	5	50% solution	12.2	1000	12.8	78.1			Good
			9.95	810	11.2	72.4	2.75		Very good
			4.90	530	19.1	27.8	2.64	12–3	Good
			3.21	450	34.5	13.1	2.45		Fair
Dextrin Comm.	5	50% solution	12.4	605	20.3	29.8			Stick
			10.0	590	30.3	19.4	1.71	15–6	Good
			7.30	440	42.3	10.4	2.38		"
Corn flour	2	Dry powder	12.5	530	43.1	12.3			Good (appear stronger than actually are)
			8.93	475	50.2	9.50			
			6.98	380	60.7	6.30		15–1	
			0.80	55					
Corn flour	5	Dry powder	11.8	890	12.1	73.5	1.15		Good
			7.96	780	15.3	50.8		15–1	Some laminated
			4.81	525	23.0	23.0	1.13		Good
			1.50	180					"
Wax	5	Water emulsion	11.8	45.0		**			Good (weak plastic strength)
			7.90	43.5			0.23	15–1	
			5.73	38.4					
			1.45	28.7			0.24		

* Bars laminated on drying; results not valid.
† With less than 5% water at pressing, granules keep identity causing unsatisfactory bars.
‡ Bars decomposed on standing; tumbling loss not determined.
§ Samples disintegrated, leaving inadequate amount intact for test.
‖ Average value from four bars; bars laminated on drying.
** Wax unsatisfactory in tumbling test; blocks and dust ball up.

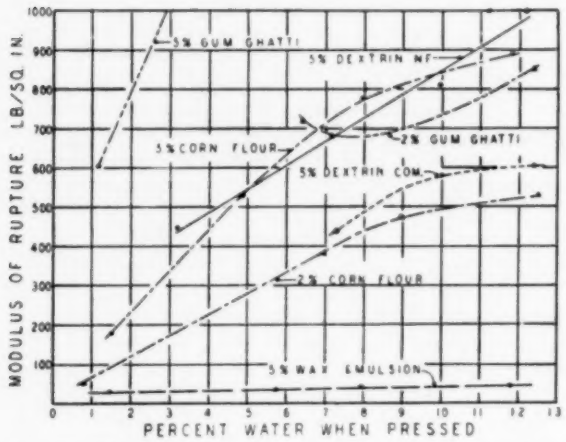


FIG. 2.—Modulus of rupture vs. water content when pressed for carbohydrate binders.

quartz grains to flow together during pressing thus giving rise to relatively high strength at very low water contents.

(2) Tumbling

In many respects, the results of modulus of rupture determinations do not give a satisfactory picture of the resistance of dry bodies to fracture.

A tumbling test was devised to measure the resistance of the samples to continuous impact. The procedure was as follows: Approximately 900 gm. of each sample in the form of bars, $1^1/_8$ by 1 by 2 in., obtained from the broken bars in the modulus of rupture test, were placed in an 8-in. internal-diameter ball mill. To this sample was added an equal weight of flint pebbles, each having approximately the same weight as a sample block. The mill was revolved and, at the end of 500, 1000, 2000, 3000, and 5000 revolutions, the charge was removed and the percentage loss in weight of the blocks was determined.

As the bars assume a spherical shape, it becomes more difficult to break particles away by impact. The weight-loss curves thus tend to flatten out, becoming appreciable after a loss of approximately 30%. At 5000 revolutions, the percentage-loss values show sufficient spread to differentiate one binder from another, and further tumbling is, therefore, unnecessary. The very soft samples also tend to disintegrate completely, after 5000 revolutions. Typical results of this test are shown in Fig. 3.

Figure 4 presents curves showing percentage loss in weight after tumbling for 5000 revolutions versus water content when pressed. In general, these results substantiate those of the modulus of rupture test. The trend of resistance to impact with changing water content at pressing is almost the same as the trend of modulus of rupture values shown in Figs. 1 and 2.

There are some exceptions to the general correlation between modulus of rupture and impact. For example, 5% peptone shows a greater loss at low water content than at high water content while the reverse is true for the modulus of rupture results. Dextrin (N. F.) at 5% concentration exhibits a minimum loss at ap-

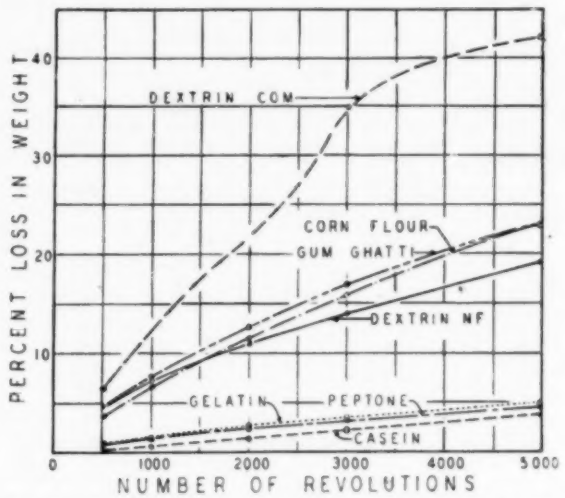


FIG. 3.—Loss in weight on tumbling vs. number of revolutions of mill.

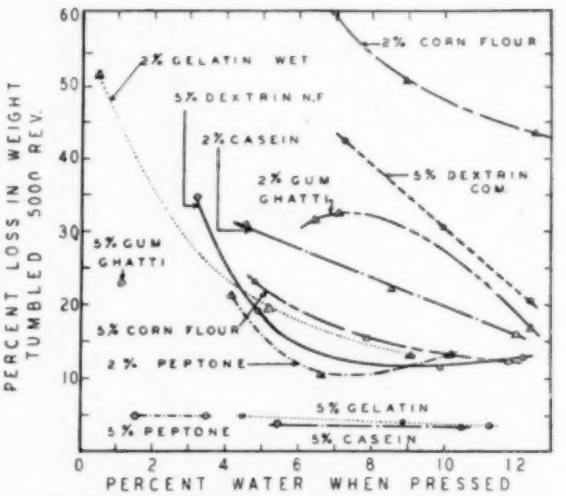


FIG. 4.—Loss in weight after 5000 revolutions vs. water content when pressed.

proximately 9% water when pressed, whereas the modulus of rupture values for the same series shows a straight-line function.

Peptone at both 2 and 5% concentrations shows greater resistance to impact (less loss on tumbling) than the modulus of rupture results indicate.

It is felt that the results of the tumbling test give additional information about binders which is not obtainable from the modulus of rupture test alone. From a practical standpoint, the results give some indication of the behavior of ceramic ware during handling when dry.

(3) Ratio of Modulus of Rupture to Percentage Loss on Tumbling

An attempt was made to correlate the results of the modulus of rupture and the tumbling tests and, thereby, to obtain some comparative measure of the

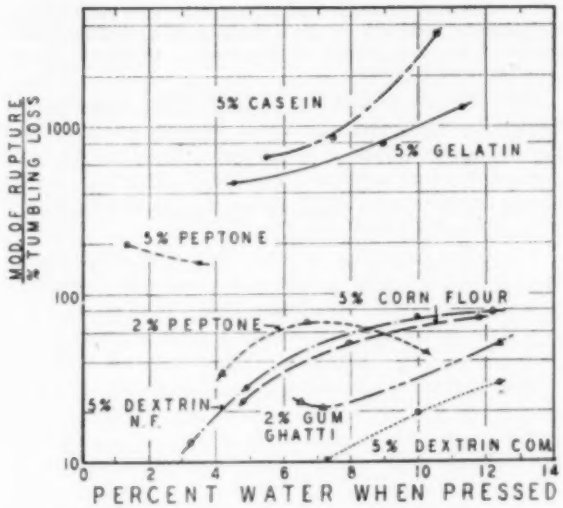


FIG. 5.—*R* vs. water content when pressed.

quality of a binder. The ratio of modulus of rupture to tumbling loss (*R*) was calculated for each binder at the various water contents; the results are given in Table II. This ratio is purely arbitrary and has no physical significance. In order to plot these results satisfactorily, it was found necessary to use a logarithmic scale on the ordinate.

It is felt that, with such results, a material can be chosen which will furnish optimum binding power at a desired water content when pressed. The higher the value of *R*, the higher the binding power; therefore, as shown by Fig. 5, it does not necessarily follow that a material which imparts higher binding strength than another at one water content is superior at all water contents. The results, furthermore, show that while the general trend is for lower values as the percentage of pressing water decreases, several binders act differently, for example, peptone and 2% gum ghatti.

While these results are closely parallel to the modulus of rupture results, especially in the appearance of individual curves, a close study will bring out many differences. For example, in Fig. 2, 5% corn flour has higher modulus of rupture values than 5% N. F. dextrin from approximately 5 to 9% of water when pressed, yet Fig. 5 shows N. F. dextrin to have superior binding characteristics in all cases studied. Another comparison might be considered, namely, 5% N. F. dextrin and 2% gum ghatti. According to the modulus of rupture values, both binders produce the same results when pressed with approximately 7% of water; yet with 7% of water in Fig. 5, the 5% dextrin value is approximately twice that of 2% ghatti.

(4) Moisture Absorption

Samples of the broken bars were placed in a humidity cabinet in which the relative humidity was maintained at 98 to 100%. The average temperature was maintained at approximately 26°C. (79°F.). Water absorption was determined daily. It was found that at the end of seven days the water absorption was essentially constant for all samples. The results are presented in Table II.

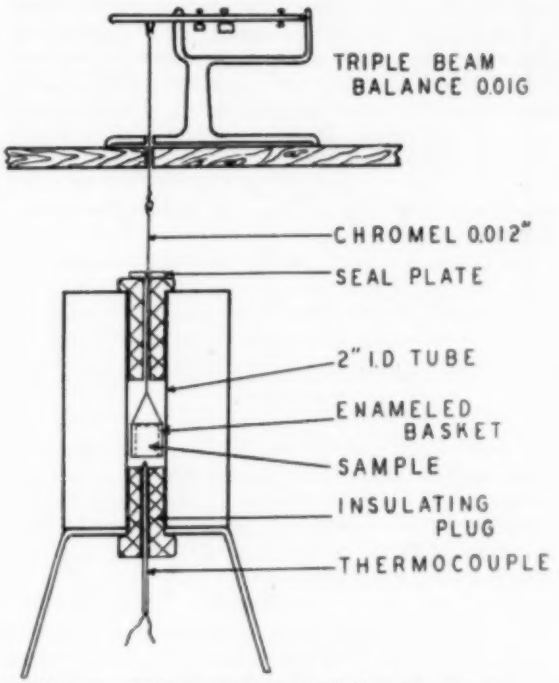


FIG. 6.—High-temperature weighing apparatus.

(5) Migration of Binder

Although a considerable amount of work was done in an attempt to develop a satisfactory determination of the degree of migration, no procedure giving quantitative results was developed. It is possible to determine migration qualitatively by cutting the bars with a grinding wheel and dipping the cut surface in various reagents which will give a color reaction with the particular organic binder being used. The depth of color obtained is a measure of the concentration of binder in the various parts of the sample. By this technique, moreover, the distribution of the binder may be determined. With the aid of a strong magnifying glass or low-power microscope, it is possible to see stained particles of a binder which have not been properly disseminated through the body. Among the staining agents which showed promise are the following:

Proteins in gelatin, casein, peptone: Saturated solution of picric acid in alcohol

Starches in flours, dextrins, etc.: Very dilute (0.05%) solution of iodine in alcohol

(6) Burn-Out

The burn-out characteristics of each binder were determined by means of a high-temperature weighing apparatus shown in Fig. 6.

A sample, weighing approximately 50 gm., was placed in the enameled metal basket, and the temperature was raised at a constant rate of approximately 1.5°C. per min. Weighings and temperature measurements were made at frequent intervals and continued until the weight became constant. The results are shown in Fig. 7.

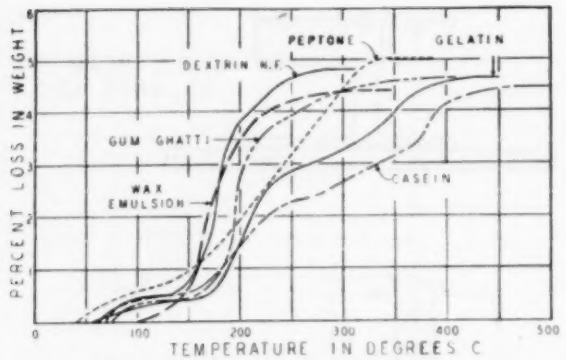


FIG. 7.—Burnout characteristics; loss in weight vs. temperature.

A study of the graph shows that as a binder burns out three distinct stages are passed through. The first occurs below 150°C. and is due to the volatilization of absorbed water. In this connection, it might be added that the weight loss in this stage is in direct agreement with the results obtained on the water-absorption test which has been discussed previously. The second stage (150° to 250°C.) represents the destructive distillation of the binder. In this temperature range, the volatile products of the destructive distillation are driven off. The final loss is believed to be due to the oxidation of the carbon residue formed by the decomposition of the binder; the temperature at which this occurs will depend on the character and particle size of the carbon present. The porosity of the sample will affect the rate of diffusion of the oxygen through the sample and thereby alter the rate of oxidation. In all cases studied, the binder was burned out at a temperature of less than 500°C.

V. Discussion of Results

The strength imparted to a body by a binder depends on (1) amount of binder used, (2) nature of constitution of binder, (3) surface attraction between the molecules of the binder and the mineral grains, and (4) amount of water present in the body when it is formed.

(1) Nature of the Binder

Natural substances possessing binding and adhesive characteristics may be classified into two main groups, the proteins and the carbohydrates.

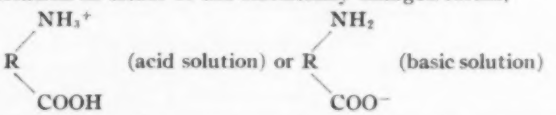
The proteins consist of carbon (50 to 55%), oxygen (25 to 30%), nitrogen (15 to 19%), hydrogen (7%), and frequently sulfur and phosphorus.* According to Bogue,† the proteins are classified into three major categories:

1. "Simple proteins—these are naturally occurring proteins which on hydrolysis decompose only into alpha-amino acids or their derivatives." (Gelatin is an example of this group.)
2. "Conjugated proteins—these are compounds of proteins with some other non-protein group. The other group is generally acid in nature." (Casein is an example of this group.)
3. "Derived proteins—this group includes all the decomposition products of the naturally occurring proteins, produced by any means whatsoever." (Peptone is an example of this group.)

The protein molecule (or molecular complex) is formed by the condensation of various amino acids. The condensed amino acids impart to the proteins very high molecular weights. The predominating active groups in the protein molecule are the amino (NH_2) and the carboxyl (COOH) groups.

A solution of protein in water may vary in character from a fluid solution (peptone) to a cloudy dispersion (gelatin). In order to obtain casein in a water solution, it is necessary to make the solvent slightly basic, preferably with ammonia. The ammonia can, of course, be replaced by caustic potash, soda, or any other alkali, but the presence of such alkalis renders the casein more sensitive to moisture.‡ Such alkalis, furthermore, will remain as an impurity in the body, whereas the ammonia will volatilize on heating.

A substance will dissolve in a fluid when the forces of attraction between its own molecules are less than the forces between these and the molecules of the fluid. In the case of an organic substance, the chemical nature of its groups is the factor which determines solubility. Increasing the hydrogen- or hydroxyl-ion concentration increases the solubility of the proteins by increasing their degree of ionization. The proteins may exist in solution as either of the electrically charged forms,



With electrically neutral protein solutions, the viscosity is at a minimum, but with electrically charged particles, for example, gelatin and casein, the molecular aggregates formed result in higher viscosity.

The increase in the tendency of proteins to form molecular aggregates as the solution becomes more concentrated is clearly illustrated if a solution of a protein is allowed to evaporate to dryness. The solubility of pure proteins is usually low; nevertheless, they do not usually separate from a water solution as a result of concentration.

If a solution of a crystalloid is evaporated to supersaturation, the dissolved substance normally starts to form a solid phase. On the concentration of a protein solution by evaporation, it is only in a few limited cases that there is any separation. The dissolved protein, clinging tenaciously to the last traces of water, forms a continuous mass of aggregated protein particles and is finally obtained as a horny, semitransparent mass of material. Drying proteins not only cling to themselves but also to many other substances with which they may be brought into contact.

The term "carbohydrate" is given to any one of a group of compounds composed of carbon, hydrogen, and oxygen with the ratio of hydrogen to oxygen usually 2 to 1. They are neutral compounds comprising the sugars, starches, celluloses, gums, etc.[14]

* See Lloyd, p. 2, footnote 5.
† See Bogue, p. 18, footnote 2.
‡ See Scherer, p. 111, footnote 3.
[14] N. A. Lange, Handbook of Chemistry, 5th ed., p. 1641. Handbook Publishers, Inc., Sandusky, Ohio, 1944.

When starch grains are treated with hot water, they swell and burst and then form a colloidal dispersion in water. The temperature at which this takes place varies from 55° to 85°C., depending on the starch used. Starches on breaking down form a compound known as amylopectin which forms a mucilaginous mass with water. No doubt, starches owe their binding power to this compound.

Dextrin is a material which is used in industry as a binding agent. Technically, the term "dextrin" comprises the degradation products of starch of the general formula $(C_6H_{10}O_5)_n$, which are soluble in hot and cold water, insoluble in alcohol and ether, almost unfermentable, and give either a red color or no color with iodine.* In the industrial sense, however, the term "dextrin" is applied loosely to denote the various products obtained by roasting starch either alone or with a small quantity of acid. These products are more or less soluble in cold water, almost completely soluble in hot water, and, in addition to dextrin, they contain more or less soluble starch and sugar.* The commercial dextrin used in this work may be considered to represent the latter definition, whereas N. F. dextrin may be considered to be of the former type.

Gums are complex carbohydrates known technically as polyuronides with active carboxyl as well as hydroxyl groups. On mixing with water, a "gum" may either slowly dissolve to give a sticky solution or it may swell up by imbibing many times its volume of water to give a gel or viscous solution. It was found in this work that gum ghatti has a greater binding power than the other carbohydrates but not as great as the simple and conjugated proteins. This also is in agreement with its composition which, in regard to active groups, is between the carbohydrates and the proteins.

In a class of materials, such as the proteins, the binding power is proportional to the chain length of the molecular complex and also to the degree of degradation or hydrolysis. A gelatin with an average molecular weight of 100,000, therefore, should have a greater binding power than a gelatin with an average molecular weight of 50,000. A high molecular weight material, such as gelatin, should also produce a stronger bond than a lower molecular weight material of the same family. That this is the case is shown by the results of this work.

The corn flour used contained 83% carbohydrate and 8.3% protein (see Table I). The protein in the flour is a simple protein (zein) and behaves in a manner similar to gelatin. The carbohydrates present may be compared with commercial dextrin. If, then, the modulus of rupture o 5% corn flour with 5% of water when pressed is calculated on the basis of its composition using the modulus of rupture values for gelatin and for commercial dextrin at the same water content, a value of approximately 600 lb. per sq. in. is obtained. The actual modulus of rupture, determined with a transverse-strength machine, is 550 lb. per sq. in.

* See Eynon and Lane, p. 191, footnote 6.

(2) Mechanism of Adhesion

Bonding or adhesion between a liquid and a solid may be considered to be of two types, (1) a mechanical bonding, which occurs only with a porous solid and is due to the penetration of the liquid into the pores of the solid, and (2) specific bonding which occurs with smooth, nonporous surfaces and is due to an interaction between the surface and the adhesive. This paper is concerned only with the second type.

Specific bonding is due to two factors, (1) the wetting of the surface of the solid by the binder as a liquid, a solution, or an emulsion, which brings the adhesive into molecular contact with the surface of the solid, and (2) an adsorption of certain active groups on the surface of the solid. It is a well-known fact that such groups as hydroxyl, carboxyl, amino, and other similar groups are readily adsorbed by the nonmetallic minerals.†

VI. Conclusions

Binding strength of organic compounds in ceramic materials is due to the presence of active groups capable of being adsorbed on nonmetallic surfaces and it is roughly proportional to the chain length of the molecular complexes. Wetting of the solid surfaces by the binder in a liquid condition is a prerequisite for proper adsorption. The actual strengths obtained from the use of organic binders is, in general, proportional to the water content of the body at forming.

A measure of resistance to impact and abrasion may be obtained by subjecting samples of the dry body to a tumbling test. Results of this test give further information regarding the strength and behavior obtained from the use of certain binders.

From a knowledge of the constitution of organic materials, it is possible to predict in some measure the possibilities of a material as a binder.

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† See Adam, footnote 9; McBain and Lee, footnote 10; and McBain and Hopkins, footnote 11.

DETERIORATION OF GLASS IN TROPICAL USE*

By Frank L. Jones

Abstract

Glass deteriorates rapidly in tropical regions with a high relative humidity. Transparency decreases due to the growth of deposits of corrosion products, chemical decomposition of the surface layer to produce pits or holes, or contamination of the surface by organic material. The processes involved in tropical deterioration are similar to the chemical reactions of glass and water in other environments.

I. Introduction

The materials most frequently involved in the deterioration of glass are water in the liquid or vapor states and aqueous solutions. The chemical factors governing the deterioration of glass in the tropical regions of the earth do not differ qualitatively from those encountered in temperate climates. The extent of the damage, however, is greater because the contact with water is increased and because the high humidity favors the growth of plant and insect life containing a large percentage of water.

II. Water Attack

In the presence of high concentrations of water vapor, the more soluble constituents of the glass migrate to the surface. If the amount of liquid water present on the surface is too little to dissolve the resulting hydroxides and carbonates, a slushy layer of crystals is formed. The loss in transparency may be slight in the case of a soda-lime-silicate window glass that forms scattered crystals of visible size, or the loss may be great in the case of a lead silicate glass where the crystals are microscopic in size and cover the surface completely. The rate of dimming depends on the composition of the glass. One month of exposure to humidity conditions of the type found in a tropical warehouse during the rainy season will cause barely visible dimming of the most durable glass compositions and will cause the most unstable glass compositions to become translucent instead of transparent.

III. Alkaline Solution Attack

Under exceptional conditions, the exact amount of water may condense on a glass surface to form a concentrated solution of the alkali salts that dissolve from the glass. The polished surface in this case becomes pitted or etched as the concentrated alkaline solution attacks the silica of the glass.

IV. Acid Solution Attack

Since the atmosphere contains a small amount of carbon dioxide, it is normal for rain or other forms of water condensed from the air to be weak solutions of carbonic acid. If a glass surface is frequently rinsed by rain or dew, the soluble salts will be carried away from the glass. Under such circumstances, a glass containing more than approximately 60% of silica or other network-forming oxides will not normally become less transparent. Glasses containing a smaller percentage of network-forming constituents and high percentages of divalent elements may become etched. The divalent ions from the glass go into solution and are replaced by hydrogen ions from the weakly acid water. A hydrated silica surface layer results. If the layer is one micron or more in thickness, it is likely to shrink sufficiently on subsequent drying to shatter the surface of the glass. A hole produced by acid attack is easily recognized since the polished glass around the defect appears colored when light is reflected from the surface. The iridescence is an interference phenomena produced by a hydrated silica surface film too thin to spall away from the glass.

V. Fungi and Other Living Organisms

A tropical environment is often characterized by a profusion of plants and animals. Foreign material that collects on a glass surface is organic in nature and contains a high percentage of water. If organic matter is present to use as food, the simple forms of plant and animal life may grow vigorously on a glass surface and render it nontransparent. Fungus or mold will obscure vision through a lens in a week if conditions are favorable. Mites or other almost microscopic insect-like animals may live and die on a glass surface until the bodies and the products of their life processes will dim vision through the glass. Plant and animal life are commonly found associated since mites feed on fungi and fungi grow on dead mites. Fungi produce organic acids that cause etching of glasses subject to acid attack. On alkali-lime-silicate glasses, fungi sometimes produce alkali-type etching by maintaining the right water supply to produce a concentrated solution of sodium or potassium carbonate. If the fungi are cleaned from a glass surface before they can take part in chemical reactions, the glass is not damaged.

VI. Conclusions

The chemical reactions involved in tropical deterioration are similar to those involved in chemical reactions between water and glass in nontropical climates. The best methods for preventing tropical deterioration involve protection from moisture during shipping and storage plus frequent cleaning of exposed glass surfaces during use.

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